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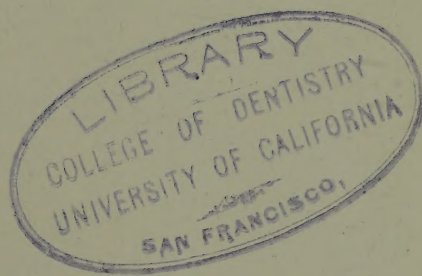
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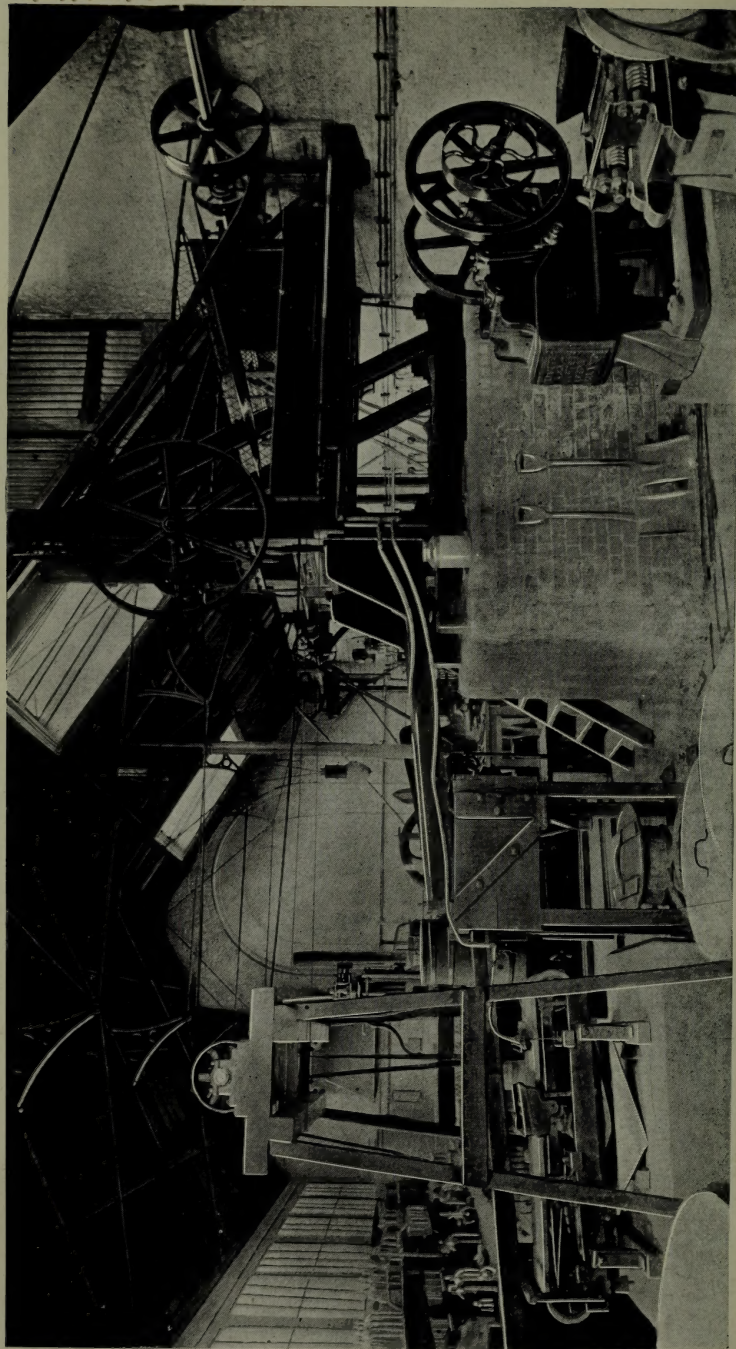
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PORTION OF THE METALLURGICAL LABORATORY AT THE ROYAL SCHOOL OF MINES, IN WHICH APPLIANCES USED FOR ILLUSTRATING THE LECTURES ARE INSTALLED.



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OF

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BY

SIR W. C. ROBERTS-AUSTEN,

F.R.S., D.C.I., D.Sc., F.R.S.,

LATE ASSOCIATE OF THE ROYAL SCHOOL OF MINES: CHEMIST AND ASSAYER OF THE ROYAL MINT.

PROFESSOR OF METALLURGY IN THE ROYAL COLLEGE OF SCIENCE, WITH

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FORMERLY CONSULTING SMELTERMASTER AND ANALYTICAL CHEMIST TO THE INDIAN  
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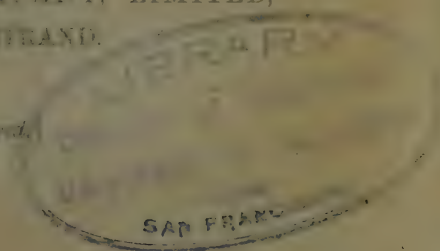
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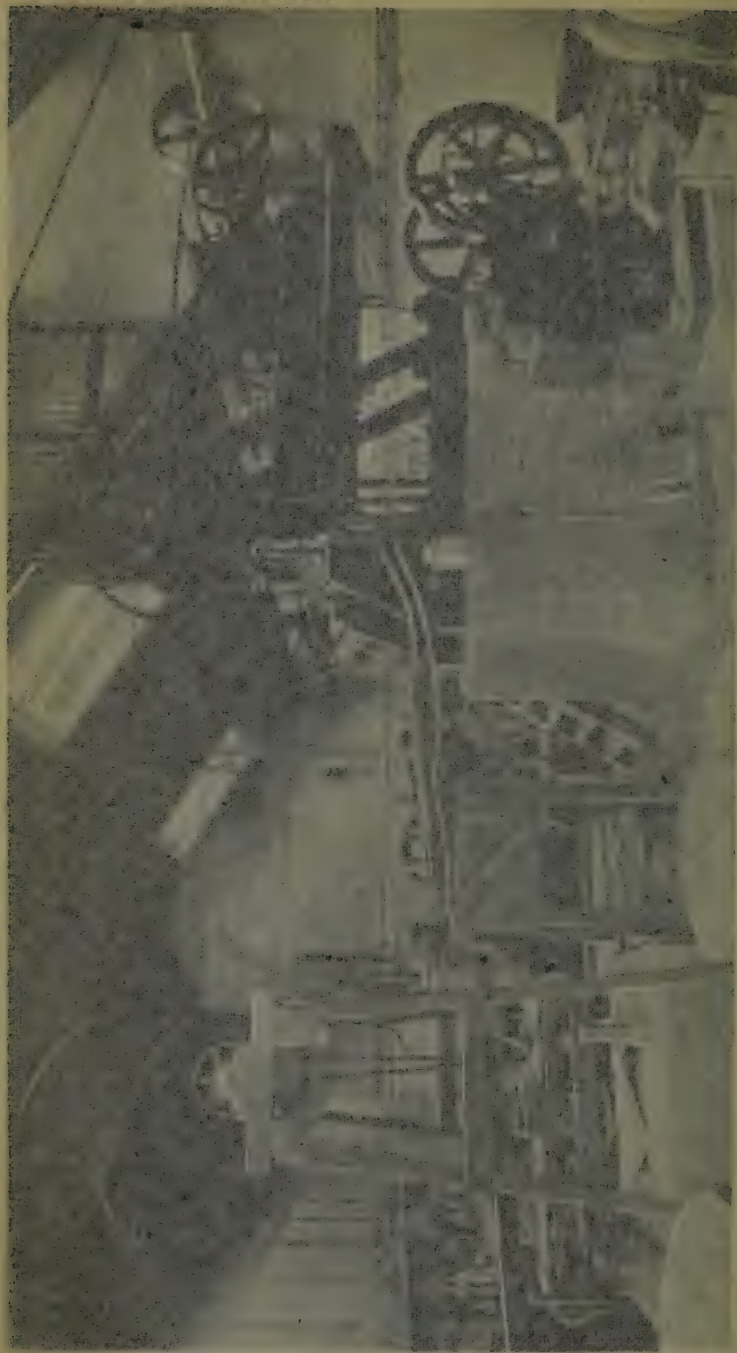
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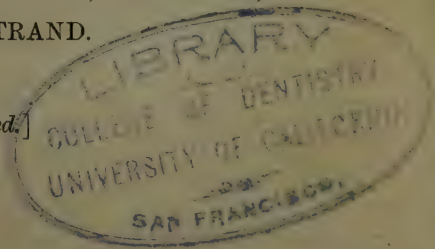
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"I rather open, than discover things."

MONTAIGNE'S ESSAYS (1580).

"No doctrine of any importance can be transferred  
in a matured shape into any man's understanding from  
without: it must arise by an act of genesis within the  
understanding itself."

DE QUINCEY (1823).

"To know

Rather consists in opening out a way  
Whence the imprisoned splendour may escape,  
Than in effecting entry for a light  
Supposed to be without."

BROWNING'S "PARACELSUS" (1835).

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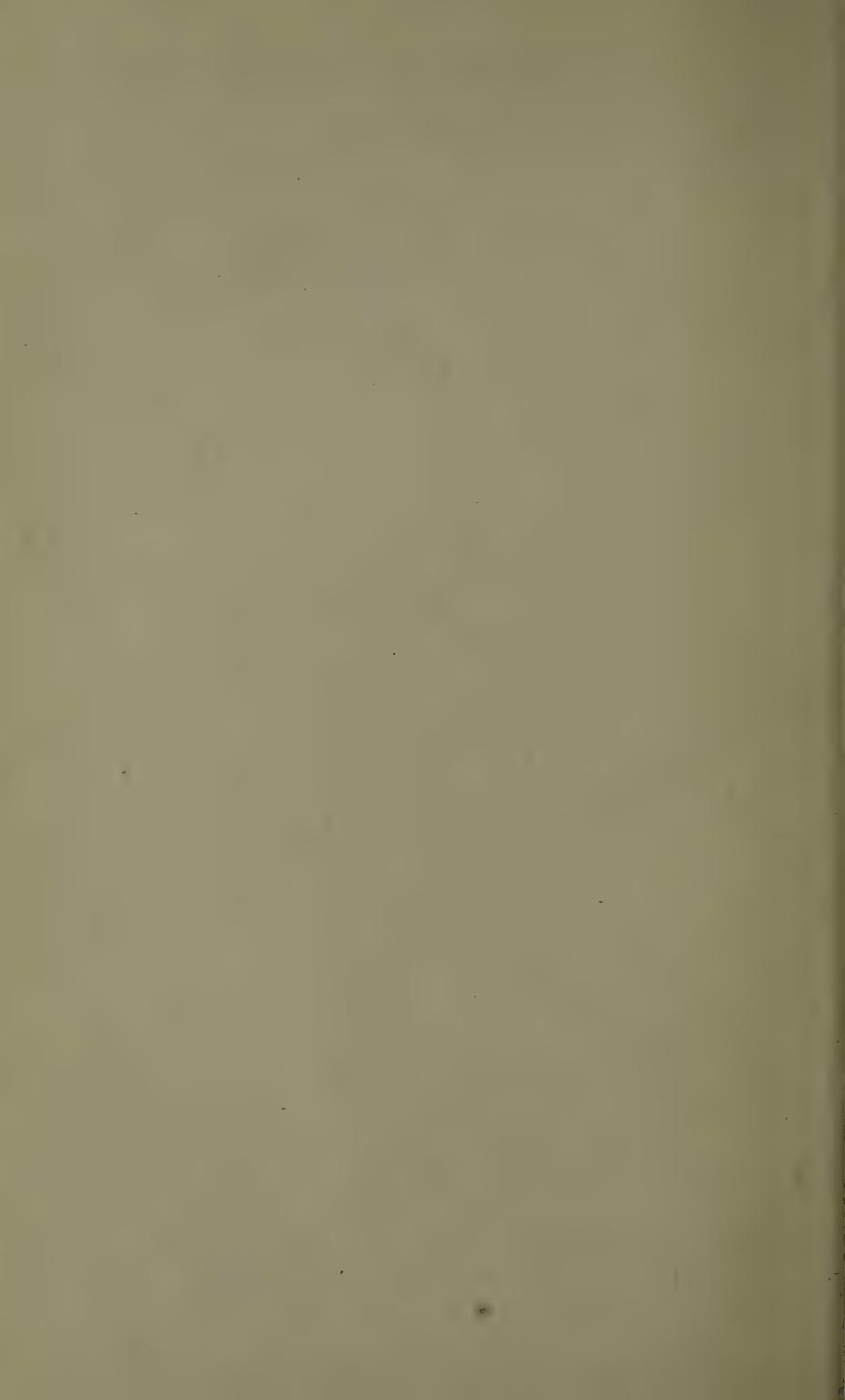
TO THE

HON. SIR C. W. FREMANTLE, K.C.B.,

DEPUTY-MASTER OF THE MINT.

FOR more than twenty years there have been few things, except this dedication, about which I have not consulted you. The book embodies the results of many investigations conducted in the Mint during that period, and the encouragement you have always given to research, and your interest in its progress, have been most helpful. This is, however, only one of the many reasons why this slender gift is so gladly offered to you, as it is now, with the sincere friendship of

THE AUTHOR.



## PREFACE TO THE SIXTH EDITION.

It was with considerable diffidence that, at the request of the Publishers and various friends of my old Professor, Sir Wm. Roberts-Austen, I undertook to prepare a new Edition of this work. It is now eight years since the last edition was published; and although I have endeavoured to preserve the general scheme of the work and to make as few alterations as possible, the results of recent research and general Metallurgical Progress have made certain revisions and additions inevitable.

Some additions have been made to Chapter II., the table of Physical Constants has been revised in accordance with the latest available data, and it has been thought desirable to transfer all matters relating to Alloys to Chapter III., which deals specially with this subject. Chapter IV., which was confined almost exclusively to the thermal treatment of steel, now includes the thermal treatment of certain industrial alloys.

Such rapid progress has been made in pyrometric work that it has been considered necessary practically to rewrite the Chapter on Pyrometry, and a new Chapter on Metallography has been prepared to replace Chapter XI. on Microstructure in the last edition.

The subject of Fuel has been given a chapter to itself instead of being discussed in connection with thermal measurement, and this chapter is illustrated by types of modern Coking Ovens and Gas Producers. In the Chapter on Furnaces, sketches of typical Furnaces used in modern metallurgical practice have been introduced as illustrations to replace those of furnaces which are no longer in general use, and sketches of some of the principal types of Electric Furnaces have also been added.

I am greatly indebted to Mr C. O. Bannister, Head of the Department of Metallurgy, Sir John Cass Institute, not only for most valuable assistance in revising the proofs and seeing the book through the press, but also for many suggestions and criticisms, and he is entirely responsible for the Chapter on Metallography, which he very kindly undertook to prepare during my absence in South Africa. I also desire to thank Professor Gowland for the sketches of different furnaces with which he supplied me, and various friends to whom I am indebted for information and assistance.

F. W. HARBORD

16 VICTORIA STREET, S.W.



## PREFACE TO THE FIRST EDITION.

THE literature of metallurgy is rich, but those who are beginning to study it need guidance to a knowledge of the principles on which the art is rightly practised. It depends, as is well known, on the application of chemistry, physics, and mechanics; but the methods of metallurgists vary greatly from those of chemists, who, however, frequently fail to appreciate the nature of the difference.

Ten years' experience has convinced me that it is more important at the outset for the student to know what was the scope of mind of the early practisers of metallurgy, and to see what kind of aid the art may be expected to receive in future from the sciences, than to acquire familiarity with complicated details of processes and appliances. In this little volume I have, therefore, devoted four chapters to these branches of the subject, embodying in them portions of lectures which I have delivered from time to time.

In all English works on metallurgy, the important metals are dealt with separately and in detail. In this, however, an attempt has been made to treat the subject as a whole, giving no minute descriptions of processes, but choosing typical appliances and indicating their use in connection with groups of metals. Such a method was adopted by the late M. Gruner, Professor of Metallurgy at the *École des Mines*, Paris, to whom I have reason to be grateful, for I have closely followed him in my class lectures.

The student will, I trust, be led to study the works in which the extraction of metals from their ores and fitting them for use are fully discussed. Such are the classical treatises of Percy, the

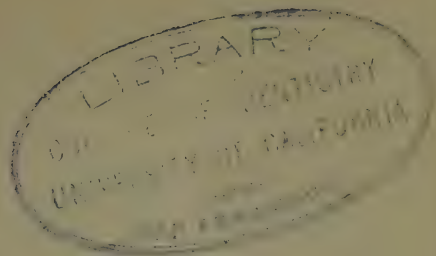
monographs of Sir Lowthian Bell, and the manual of Phillips and Bauerman, from which volume a few illustrations have been borrowed. The literature of the subject has been enriched by Howe, of Boston, who has collected a store of facts in his elaborate and recently published volume on steel.

In the preparation of a portion of this little work, I have been aided by my colleague, Mr Bennett Brough, whose help has been specially useful in passing the work through the press.

I hope that the book will be found useful to my own students, for whose progress I feel sincere solicitude.

CHILWORTH, SURREY,

*December 23, 1890.*



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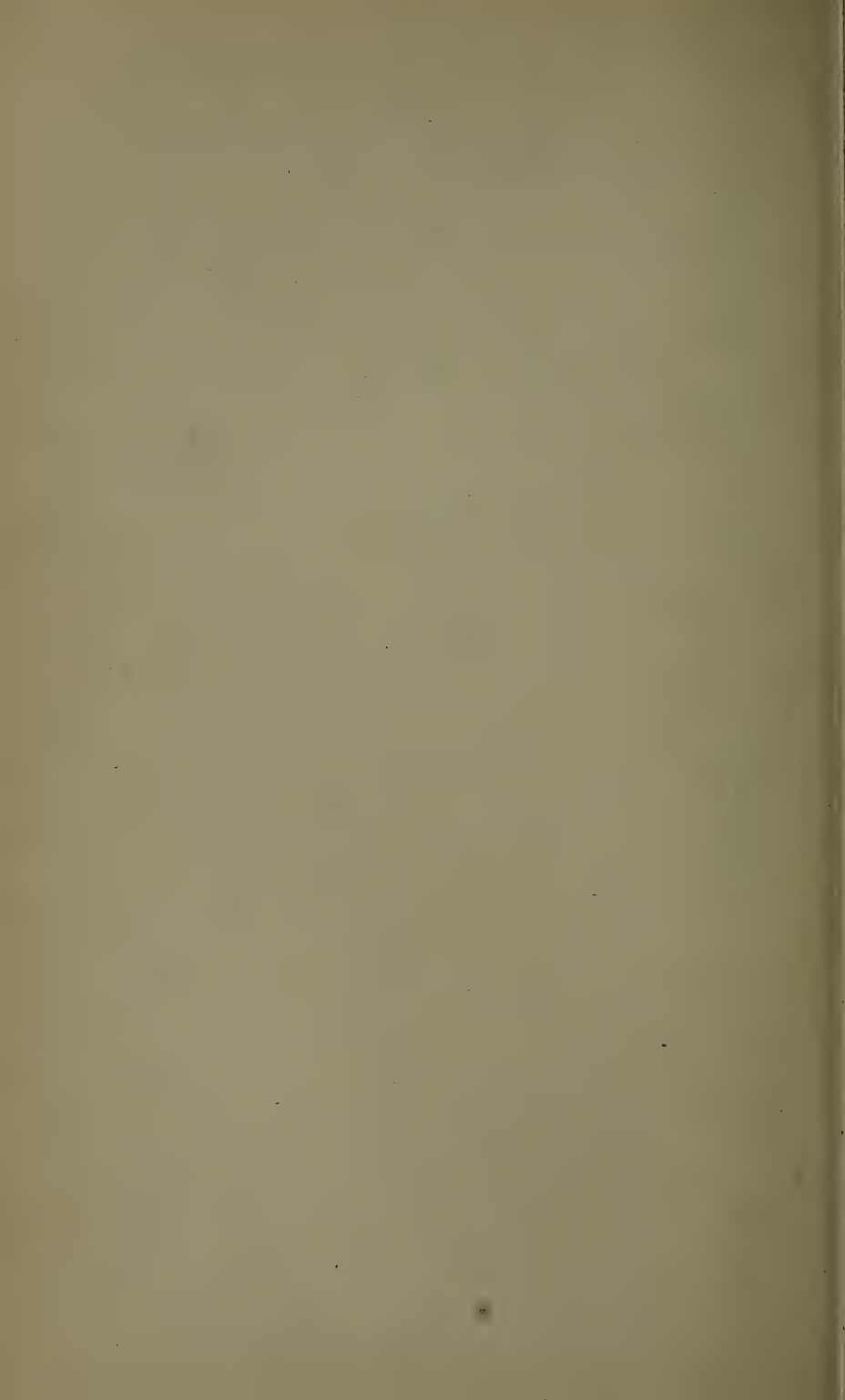
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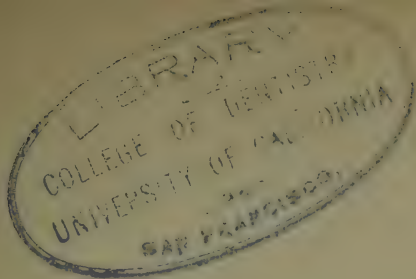
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May 10  
1885

# INTRODUCTION TO THE STUDY OF METALLURGY.

## CHAPTER I.

### THE RELATION OF METALLURGY TO CHEMISTRY.

THE distinguished metallurgist who may be said to have created the English literature of the subject concluded the introductory lecture he delivered<sup>1</sup> at the Royal School of Mines by pointing out to the students who were then beginning their course, that "in proportion to the success with which the metallurgic art is practised in this country, will the interests of the whole population, directly or indirectly, in no inconsiderable degree, be promoted."

During the period of more than fifty-five years since Dr Percy began to teach, the conditions under which metallurgy is practised have changed considerably; for the field of knowledge has so widely extended, the scale on which operations are conducted is now so great, and the mechanical appliances they involve are so varied and complicated, that while the interest of the subject is deepened, its difficulty is gravely increased. Metallurgy involves not only a knowledge of "the art of extracting metals from their ores," but also of the means of "adapting them for use," which is effected by complicated mechanical operations, and, strange as it may seem, by varying the degree of purity, often to a very slight extent. It will thus be evident that the student must possess adequate knowledge of Inorganic Chemistry, Mechanics, and Physics. Besides this, he must acquire aptitude for dealing with economic details.

**Historical Sketch.**—In turning to the history of metallurgy, it is easy to be led away by the charm of the antiquarian store of riches into devoting too much time to literary research. It should

<sup>1</sup> *Records of the School of Mines*, vol. i. pt. i. (1852), p. 127.

be remembered, however, that much of what is both interesting and full of suggestion, even at the present day, is to be found buried in the treatises by the old writers whose work we inherit and continue.

Primitive metallurgical processes are referred to in some of the oldest known historical records; naturally, therefore, the scientific development of metallurgy must have been long preceded by its empirical practice as an art, an art for which a place has even been claimed among the religious systems of antiquity.<sup>1</sup> The earlier literature of the subject consists mainly of descriptions of processes; but it is well known that chemistry was to a great extent built up on a metallurgical basis, and Black's singularly advanced definition of chemistry as the "effects produced by heat and mixture"<sup>2</sup> might well be applied to metallurgy. The library of Leyden contains a papyrus which has been described by M. Reuven's,<sup>3</sup> and which is considered by Kopp<sup>4</sup> to be the oldest known chemical manuscript, its date being possibly as early as A.D. 200. It treats generally of metallurgical matters, and the purification of gold and silver is frequently mentioned. Of all chemical phenomena, probably none have more contributed to advance chemistry as a science than those bearing upon the relations between oxygen and lead; and the interest attaching to the mutual behaviour of these two elements is so great that the student will do well to consider the influence of one very ancient metallurgical process on the scientific views of the present day.

When lead is melted with free access of air, a readily fusible substance forms on its surface. This substance may be allowed to flow away, or, if the metal is contained in a suitable porous receptacle, the fusible oxide sinks into this containing vessel; in either case the oxidation of the lead affords a means of separating it from precious or inoxidisable metals, if any were originally present in the lead. The above fact has been known from remote antiquity, and the early Jewish writers allude to it as old and well-known. They clearly show, for instance, that lead can be removed from silver by being "consumed of the fire," while the silver is not affected. That the Greeks knew and practised this method of *cupellation* is abundantly proved, if only by certain specimens of gold and silver which were discovered by Dr Schliemann on the site of ancient Troy. The Arabians investigated the subject, as is shown by the writings of Geber,<sup>5</sup> the greatest of the early chemists (he died in 777), who gives a remarkable account

<sup>1</sup> Rossignol, *Les Métaux de l'Antiquité* (1863).

<sup>2</sup> *Lectures*, by Joseph Black, M.D., vol. i. pp. 11, 12 (Edin. 1803).

<sup>3</sup> Reuven's, *Lettres à M. Lefronne* (Leyden, 1830), quoted by Prof. Ferguson in an address to the Glasgow Phil. Soc. (1876), p. 19.

<sup>4</sup> *Beiträge zur Geschichte der Chemie*, 1869.

<sup>5</sup> The works of Geber, translated by R. Russell (1686), pp. 74, 78, 220, 234.



of cupellation; he also describes the conversion of lead into a fine powder by calcination with much clearness, and he noticed the fact that after calcination the mass has "acquired a new weight in the operation." His subsequent observations on the reduction of altered metals from their "calxes" show that he knew the weight to be increased; in any case it is interesting to remember that his work was, in a sense, quantitative. He, moreover, was cognisant of the fact that two different substances may be produced by heating lead in air, and he assumed that "in the fire of calcination a fugitive and inflammable substance is abolished." The alchemists refer continually to the subject, and "deliver themselves," as Roger Bacon said in his *Speculum Alchimie*, "in the enigmas and riddles with which they clouded and left shadowed to us the most noble science." Eck of Sulzbach showed (1489) that metals augment in weight by calcination, and that what we now call red oxide of mercury gives off "a spirit" when heated; had he named and isolated the spirit, he would have discovered oxygen. The great metallurgist of the sixteenth century, Agricola,<sup>1</sup> points out that lead increases in weight when it is exposed to the action of moist air. In the middle of the sixteenth century, the equally accomplished metallurgist, Biringuccio,<sup>2</sup> contemporary of Paracelsus and Agricola, seems to have been specially attracted by the phenomenon in question, and he remarks:—"If we had not lead we should work in vain for the precious metals, for without its aid we could not extract gold or silver from the stones containing them. . . . The alchemists also," he says, "make use of it in their operations, calcining it by itself or with other substances; but," he goes on to observe, "the calcination, conducted in a reverberatory furnace, is accompanied by a marvellous effect, the result of which should not be passed by in silence, for lead thus treated increases 10 per cent. in weight, and considering that most things are consumed in the fire, it is remarkable that the weight of lead is increased and not diminished." Although he subsequently gives evidence of much accurate knowledge of practical metallurgy, his views as to this particular phenomenon were hardly in advance of Geber's; but we may claim Biringuccio as an early metallurgist, who knew the facts and recognised that they were theoretically important. Cæsalpinus, in his work *De Metallicis*, showed that the film which covers lead exposed to moist air and augments its weight is due to an aeriform body. It was not till nearly a century later (1630) that a French chemist, Jean Rey,<sup>3</sup> stated that the increase in weight came from the air. The problem attracted much attention in England, and it is not a little interesting that among the very

<sup>1</sup> *De ortu et causis subterraneorum*, p. 519.

<sup>2</sup> *Pirotechnia* (Venezia, 1540), translated into French by T. Vincent (Rouen, 1627), p. 41.

<sup>3</sup> *Essais de Jean Rey* (reprinted in Paris, 1777), p. 64.



first experiments recorded by our own Royal Society is a metallurgical series relating to the weight of lead increased in the fire on the "copels" at the assay office in the Tower, the account being brought in by Lord Brouncker in February 1661.<sup>1</sup> Subsequently, in 1669, John Mayo showed that the increase in weight of calcined metals was due to a "spiritus,"<sup>2</sup> derived from the sun's rays.<sup>3</sup> Nevertheless, Boyle heated lead in a small retort,<sup>4</sup> and attributed the increase in weight, as Lemery also did,<sup>5</sup> to his having "arrested and weighed igneous corpuscles." One of the most curious passages known is in the *Hippocrates Chemicus* of Otto Tachen, a German who lived at Venice, and published his book there in 1666. He describes how lead, when burnt to minium, increases in weight. This increase he ascribes to a substance of acid character in the wood used for burning, and then, by a very ingenious course of argument, based on the saponifying powers of litharge, makes out that lead is of the nature of, or contains an alkali which combines with, the "occult acid of the fat." This is a curious anticipation of a very modern classification, which brings lead into relationship with the alkalies and alkaline earths, as well as of Chevreul's investigations on saponification. Cæsalpinus had previously called lead "a soap" which in cupellation washes gold and silver.

It is hardly necessary to point out how important this calcination of lead was considered by those who defended the Phlogistic theory in regard to chemical change, the theory propounded by the metallurgist Becher, which, for more than a century, exerted so profound an influence on scientific thought. His views were first embodied in the *Physica Subterranea* (1669) and in the *Alphabetum Minerale* (1682).

According to his still more famous pupil Stahl, the litharge produced by the prolonged calcination of lead in air, is lead deprived of its phlogiston; but he and his followers were indifferent to the fact that when lead is burnt the weight of the resulting mass is greater than that of the original metal, and were content to insist that the burnt lead had lost its inflammable principle—that is, Phlogiston.

Tillet, assayer of the Paris Mint, made some quantitative experiments which led up in a singular way to the work of Lavoisier, who, as is well known, overthrew the old phlogistic theory by showing that a chemical combination takes place, resulting in an augmentation of weight which represents the exact weight of the gaseous body added. At the same time it should be remembered that the phlogistic chemists made a great step in advance, as was

<sup>1</sup> MS. register book of the Royal Society.

<sup>2</sup> *Tractatus quinque Medico-Physici*, p. 25 et seq. (Oxonii, 1674.)

<sup>3</sup> Prof. Cohen, *Intrody. Lecture*, Yorkshire Coll. of Science, 1901-2.

<sup>4</sup> Collected works, vol. ii. (1744), p. 395, and vol. iii. p. 347.

<sup>5</sup> *Cours de Chymie* (1675), 2nd English edition (1686), p. 107.

admitted by J. R. Mayer<sup>1</sup> in his memoir on the mechanical theory of heat; and Odling, discussing the experiments on the oxidation of lead, has pointed out<sup>2</sup> that an error has arisen in consequence of the same word being used in a different sense at different periods of time; chemists, in fact, now substitute the words "potential energy" for phlogiston, or, as Dr Crum Brown well observed,<sup>3</sup> we recognise "that no compound contains the substances from which it was produced, but that it contains them *minus* something. We know now what this something is, and can give it the more appropriate name of potential energy; but there can be no doubt that this is what the chemists of the seventeenth century meant when they spoke of phlogiston."

It will thus be evident that the main aim of chemical investigation down to the end of the eighteenth century was the explanation of calcination, combustion, or oxidation, and that lead was especially useful in solving the problem. It might, perhaps, be added that the absorption of oxygen by molten lead furnished Ste. Clair-Deville,<sup>4</sup> a physicist and metallurgist, with an important step in the argument as to dissociation, thus connecting the history of the metal, lead, with the great advance on the borderland of chemistry and physics which has been made in modern times.

The above remarks will be sufficient to show that conclusions of the utmost importance in the history of chemical theory were based on the very ancient metallurgical process of cupellation of lead, a process which affords an appropriate illustration, because, in the gradual development of the knowledge derived in the first instance from the metallurgy of lead, there is much that is typical of the mutual relation of theory and practice that still prevails.

Now, as in the past, in the study of metallurgy, a prominent position must be given to the production of high temperatures, as it will be obvious that metallurgists have principally to consider the reactions of the elements when under the influence of heat. In the first half of the present century, temperatures higher than the melting-point of zinc had not been determined with any degree of certainty; but, in 1856, Henri Ste. Claire-Deville pointed out that chemistry at high temperature, that is to say, up to the blue-white heat at which platinum volatilises and silica fuses, remained to be studied, as under such conditions ordinary chemical reactions may be modified or even reversed. Subsequently, in conjunction with Troost, he gave certain fixed points, such, for instance, as the boiling-points of cadmium and zinc; and his

<sup>1</sup> "Bemerkungen über die Kräfte der unbelebten Natur," *Liebig's Ann.*, vol. xlii. (1842), p. 233.

<sup>2</sup> *Proc. Roy. Inst.*, vol. vi. (1871), p. 323.

<sup>3</sup> *Edin. Roy. Soc. Proc.*, vol. v. (1866), p. 328.

<sup>4</sup> "Leçons sur la dissociation," and Wurtz, *Dictionnaire de Chimie*, vol. i. (1868), p. 1174.

researches on dissociation have entirely modified the views generally entertained in regard to the theory of combustion. Indeed, so much is due to this illustrious teacher, that the best homage that can be offered to his memory will be to work in the directions he has indicated.

Dewille's experiments on dissociation have rendered it possible to extend to the groups of atoms in chemical systems the laws which govern the fusion and vaporisation of masses of matter, and this has produced a revolution comparable in its importance to that which followed the discovery of the law of definite proportions, for dissociation has shown us that true causes of chemical change are variations of pressure and of temperature. For instance, oxygen may be prepared on an industrial scale from air by the intervention of oxide of barium heated to a constant temperature of  $700^{\circ}$ , provided air be admitted to the heated oxide of barium, under a pressure of  $1\frac{1}{2}$  atmospheres, while the oxygen, thus absorbed, is evolved if the containing vessel be rendered partially vacuous. It will be evident, therefore, that at a certain critical temperature and pressure the slightest variation of either will destroy the equilibrium of the system and induce chemical change.

It will be clear that the measurement of high temperatures has become a question of much moment, and in this direction remarkable progress has recently been made.

The essential difference in the properties of metals produced by a small quantity of foreign matter introduces one very distinctive feature of metallurgy—the enormous influence exerted on a large mass of metal by a “trace” of another metal or metalloïd, that is, by a quantity so small that it appears to be out of proportion to the mass in which it is distributed; and it may safely be asserted, that in no other branch of applied science has the operator to deal with quantities that are at once so vast and so minute.

It may be that the “trace” is alone of value, as, for instance, the few grains of gold that can be profitably extracted from a ton of material, which, though containing only one part of gold in five millions by volume, is thereby entitled to be regarded as an auriferous deposit that can be profitably worked; or it may be that the presence of a minute percentage of a metalloïd is prejudicial and must be extracted, in order that the physical properties of the remaining mass of metal may not be such as to render it useless. Due prominence is given to such facts in the following pages.

It is assumed throughout that the student possesses a certain amount of chemical knowledge, but it will be evident that Metallurgical Chemistry is a special branch of chemical science which does not come within the ordinary sphere of the academic teaching of chemistry. It is often urged that metallurgical



practice depends upon the application of chemical principles which are well taught in every large centre of instruction in this country, but a long series of chemical reactions exist which are of vital importance to the metallurgist, though they are not set forth in any British manual of chemistry, nor are dealt with in courses of purely chemical lectures. It is well to insist upon this point, because purely analytical and laboratory methods are so often given in the belief that they are applicable to processes conducted on a large scale and at high temperatures.

It is urged that technical instruction should be kept apart from scientific education, which consists in preparing students to apply the results of past experience in dealing with entirely new sets of conditions, but it can be shown that there is a whole side of metallurgical teaching which is truly educational, and leads students to acquire the habit of scientific thought as surely as the investigation of any other branch of knowledge.

It is, in fact, hardly possible, in a course of theoretical chemistry, to devote much attention to specific cases of industrial practice in which reactions are incomplete because they are limited by the presence of bodies that cannot be directly eliminated from the chemical system. Take, for instance, the long series of reactions studied by Plattner, who published the results of his investigations in his celebrated treatise *Die Metallurgische Röstprozesse*, Freiberg, 1856. A complex sulphide, of which copper is the main metallic constituent, contains some fifty ounces of silver to the ton, and the problem may be supposed, for the present, to be limited to the extraction of the precious metal from the mass in which it is hidden. The student deriving his knowledge from an excellent modern chemical treatise would find the case thus stated:—

“Ziervogel’s process depends upon the fact that when argentiferous copper pyrites is roasted, the copper and iron sulphides are converted into insoluble oxides, whilst the silver is converted into a soluble sulphate which is dissolved out by lixiviating the roasted ore with hot water, the silver being readily precipitated from this solution in the metallic state.”

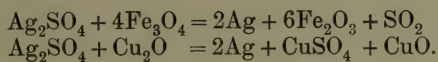
It is certain that if an observant, chemically trained student visited a silver extraction works, and possessed sufficient analytical skill to enable him to secure evidence as to the changes that occur, he would find a set of facts which his training had not enabled him to predict, and he would establish the existence of a set of reactions to the nature of which his chemical reading had hardly given him a clue. The process to be considered is a simple one, but it is typical, and applies to a considerable proportion of the silver annually obtained from cupriferous compounds. He would be confronted with a ton or more of finely divided material spread in a thin layer over the bed of a reverberatory furnace. Suppose the material is what is known

as a complex "regulus" as imported into Swansea or produced at Freiberg, to which are added rich native sulphides. The mixture then consists of sulphides mainly of iron and copper, with some sulphide of lead, and contains fifty or sixty ounces of silver to the ton, and a few grains of gold. It may also contain small quantities of arsenic and antimony as arsenides, antimonides, and sulpho-salts, usually with copper as a base.

The temperature of the furnace in which the operation is to be performed is gradually raised, the atmosphere being an oxidising one. The first effect of the elevation of the temperature is to distil off sulphur, reducing the sulphides to a lower stage of sulphurisation. This sulphur burns in the furnace atmosphere to sulphurous anhydride ( $\text{SO}_2$ ), and coming in contact with the material undergoing oxidation is converted into sulphuric anhydride ( $\text{SO}_3$ ). It should be noted that the material of the brickwork does not intervene in the reactions, except by its presence as a hot porous mass, but its influence is, nevertheless, considerable. The roasting of these sulphides presents a good case for the study of chemical equilibrium. As soon as the sulphurous anhydride reaches a certain tension the oxidation of the sulphide is arrested, even though an excess of oxygen be present, and the oxidation is not resumed until the action of the draught changes the conditions of the atmosphere of the furnace, when the lower sulphides remaining are slowly oxidised, the copper sulphide being converted into copper sulphate mainly by the intervention of the sulphuric anhydride formed as indicated. Probably by far the greater part of the iron sulphide only becomes sulphate for a very brief period, being decomposed into the oxides of iron, mainly ferric oxide, the sulphur passing off. Any silver sulphide that is present would have been converted into metallic silver at the outset were it not for the simultaneous presence of other sulphides, notably those of copper and of iron, which enables the silver sulphide to become converted into sulphate. The lead sulphide is also converted into sulphate at this low temperature. The heat is now raised still further with a view to split up the sulphate of copper, the decomposition of which leaves oxide of copper. If, as in this case, the bases are weak, the sulphuric anhydride escapes mainly as such; but when the sulphates of stronger bases are decomposed the sulphuric anhydride is to a great extent decomposed into a mixture of sulphurous anhydride and oxygen. The sulphuric anhydride, resulting from the decomposition of this copper sulphate, converts the silver into sulphate, and maintains it as such, just as, in turn, at a lower temperature, the copper itself had been maintained in the form of sulphate by the sulphuric anhydride eliminated from the iron sulphate. When only a little of the copper sulphate remains undecomposed, the silver sulphate begins to split up, and the furnace charge must therefore be immediately withdrawn,



or the whole of the silver sulphate would be converted into metallic silver, partly by the direct action of heat alone, and partly by reactions such as those shown in the following equations:—



If the charge were not withdrawn, the silver would thus be effectually removed from the solvent action of water, and the smelter's efforts would have failed entirely. The charge still contains lead sulphate, which cannot be completely decomposed at any temperature attainable in the roasting furnace, except in the presence of silica, and it is well to leave it where it is if the residue has subsequently to be smelted with a view to the extraction of the gold. The elimination of arsenic and antimony gives rise to problems of much interest, and again confronts the smelter with a case of chemical equilibrium. For the sake of brevity it will be well for the present to limit the consideration to the removal of antimony, which may be supposed to be present as sulphide. Some sulphide of antimony is distilled off, but this is not its only mode of escape. An attempt to remove antimony by rapid oxidation would be attended with the danger of converting it into insoluble antimonates of the metals present in the charge. In the early stages of the roasting it is therefore necessary to employ a very low temperature, and the presence of steam is found to be useful as a source of hydrogen, which removes sulphur as hydrogen sulphide, the gas being freely evolved. The reaction  $\text{Sb}_2\text{S}_3 + 3\text{H}_2 = 3\text{H}_2\text{S} + 2\text{Sb}$  between hydrogen and sulphide of antimony is, however, endothermic, and could not, therefore, take place without the aid which is afforded by external heat. The facts appear to be as follows: sulphide of antimony, when heated, dissociates, and the tension of the sulphur vapour would produce a state of equilibrium if the sulphur thus liberated were not seized by the hydrogen and removed from the system. The equilibrium is thus destroyed and fresh sulphide is dissociated. The general result being that the equilibrium of the system is alternately restored and destroyed until the sulphide is all decomposed. The antimony combines with oxygen and escapes as volatile oxide, as does also the arsenic, a portion of which is volatilised as sulphide.

The main object of the process which has been considered is the formation of soluble sulphate of silver. If arsenic and antimony have not been eliminated, their presence at the end of the operation will be specially inconvenient, as they give rise to the formation of arseniate and antimoniate of silver, insoluble in water, which may necessitate the treatment of the residues by an entirely different process from that which has hitherto been considered.

It will have been evident that effecting this series of changes demands the exercise of the utmost skill, care, and patience. The operations beginning at a dull red heat, or a temperature of some  $500^{\circ}$ , are completed at  $700^{\circ}$ , within a range, that is, of  $200^{\circ}$ . Judicious stirring has been necessary to prevent the formation of crusts of sulphates, which would impede the reactions, and, as has been shown, an undue elevation of temperature within a very limited range would, at any stage, have been fatal to the success of the operation. It is difficult to appreciate too highly the delicacy of sight and touch which enables an operator to judge by the aid of rough tests, but mainly from the tint of the streak revealed when the mass is rabbled, whether any particular stage has or has not been reached, and it will be obvious that the requisite skill is acquired solely by observation and experiment. The technical instructor may impart information as to the routine to be followed, and the appearances to be observed, but scientific knowledge of a high order can alone enable the operator to contend with the disturbing influences introduced by the presence of unexpected elements or by untoward variations in temperature. In the training of a metallurgist it is impossible to separate education from instruction, and the above description of a very ordinary operation will show the intimate relations between science and practice which are characteristic of metallurgical operations. Practice is dependent on science for its advancement, but scientific workers too often hesitate to attack metallurgical problems, and to devote the resources of modern investigation to their solution, because they are not aware of the great interest of the physical and chemical problems which are connected with many very simple metallurgical processes, especially with those that are conducted at high temperatures.

Proceeding yet one step further, suppose that the copper smelter takes possession of the residual mass, consisting mainly of oxide of copper, he would smelt it with fresh sulphide ores and obtain, as a slag from the earthy matters of the ore, a ferrous silicate containing some small proportion of copper. The displacement of the copper from this silicate may be effected by fusing it with sulphide of iron, a fusible sulphide of iron and copper being formed which readily separates from the slag. By this reaction some thousands of tons of copper are added to the world's annual production. Proceeding a step further, suppose the smelter to have reduced his copper to the metallic state. If arsenic had been originally present in the ore, and had not been eliminated entirely in the roasting, extraordinary difficulties would be met with in the later stages of the process, in extracting small quantities of arsenic which resist the smelter's efforts. Copper, moreover, containing above 1 per cent. of arsenic cannot be "overpoled," as the presence of arsenic hinders the action of gases on the copper. The amount of arsenic which

the copper smelter has to remove may vary from mere traces up to 1 per cent., and if the copper is destined for the use of the electrical engineer, he will insist on its being as pure as possible, for the presence of traces of arsenic would materially increase the electrical resistance of the copper, and would be fatal to its use in submarine telegraphy. If, on the other hand, the copper is intended for the maker of locomotive fire-boxes, he will encourage the retention of small quantities of arsenic, as it is found to actually increase the endurance of the copper up to 0.4 per cent., and the smelter will in such a case have no inducement to use the special methods for the removal of arsenic with which he is familiar. It may all seem simple enough, but the modern process of copper smelting has been laboriously built up, and has a long and interesting pedigree which may be traced to at least the eighth century, when Geber described the regulus "coarse metal" as being "black mixed with livid," and our familiar "blue metal" as being "of a most clean and pleasant colour," and indicated the reason for the difference.

It must not be supposed, even when commercially pure copper lies on the furnace bed, ready to be transferred to moulds, that its turbulent career of reactions is over. It might be thought that the few tenths per cent. of impurity, dissolved oxide, and occluded gas are so far attenuated by distribution that their interactions must be insignificant. This is far from being the case. The bath of metal is seething from its reactions until the copper is solid, and then polymerisation begins. There may not be a sharply defined critical range of temperature within which the metal can alone be successfully worked, which varies, as regards its starting-point, with the kind of impurity present, as is the case with steel; but evidence of molecular change in the solid metal is afforded by the pyrometric curves of cooling, to which subsequent reference will be made in this work, and by the singular behaviour, as regards electrical resistance, of various samples of copper, in which chemical analysis hardly reveals a difference.

The above description of a very ordinary set of operations will serve to indicate the general nature of the problems with which the metallurgist has to deal.



## CHAPTER II.

### PHYSICAL PROPERTIES OF METALS.

**Molecular Structure.**—The physical aspects of metals are so pronounced as to render it difficult to abandon the old view that metals are sharply defined from other elements, and form a class by themselves. The term “metal” is in fact somewhat arbitrary. Zinc and bismuth, when they were first discovered, were considered to be semi-metals, and it was not until mercury was frozen by Braune in 1759 that it was recognised as a metal. Like all other elements, metals are composed of atoms grouped in molecules, and any force that alters the relations of the atoms in the molecules modifies the physical properties of the metals. Indeed, it would be easy to show that the physical constants of each metal vary with its degree of purity. The molecular grouping of metals is doubtless very varied, and little definite is known regarding the structural stability of most of them; but it may be assumed that it is not very great, as some metals split up into single atoms when they are volatilised, and most of them unite readily with chlorine and with oxygen.<sup>1</sup> The great interest which has of late been shown in the constitution and behaviour of metals and alloys has led to important results. The fact has been recognised that many laws of physical chemistry, hitherto considered mainly in relation to chemical compounds, are found to be applicable to metals and alloys. The result is that the barrier existing between metals and alloys and the non-metallic elements and compounds is being gradually removed. It is probable that in many pure metals, such as gold, silver, copper, and iron, the individual molecules are of simple atomic constitution, and that these fundamental molecules bear a uniform relationship to one another. Consequently, any mass, of which the fundamental molecules are the constituent particles, may practically be regarded as a single molecule. Two funda-

<sup>1</sup> Lothar Meyer, *Modern Theories of Chemistry*, English translation, 1888, p. 568.

mental molecules must, however, be held to be capable of uniting to form complexes that have less power of cohering, and any circumstance tending to bring about the formation of such complexes would also tend to make the material less tough. This may account for the extraordinary alteration in the properties of many metals produced by very small quantities of incompatible foreign matters.<sup>1</sup>

**Crystalline Structure of Metals.**—This is a subject to which a considerable amount of attention has been directed in recent years. It is closely allied to and is, in fact, difficult to dissociate from the study of microstructure, which will be treated in a later chapter.

Much confusion arises from the failure to realise, at the outset, exactly what is meant by the crystalline structure. Before the microscope was adopted for the examination of metals, structure was generally understood to mean the appearance of a fractured surface which was referred to in such general terms as "fine-grained" or "coarse-grained." It is now more usual to compare structures as revealed by suitably etching a polished metallic surface. As regards the appearance of the fractured surface and the size of grain, mention should be made here of the classical work of Chernoff and of Brinell bearing on the changes in size of grain of steel under varying conditions of thermal treatment. The work of Osmond, Stead, Arnold, Howe, and others follows on similar lines, but with the aid of the microscope. Attention is drawn to the distinction between the grains of which a mass of metal is usually composed and the crystallites which compose each grain, the latter constituting the true crystalline structure. Further, it has been pointed out that in each grain the crystallites are arranged in a definite direction or orientation, and the growth of grains in soft steel as the outcome of annealing (a fact well known to steelworkers) has been considered<sup>2</sup> to be due to the orientation of the crystallites of adjacent grains becoming coincident. A wider knowledge of the conditions of growth of grains in other metals has resulted from the work of Ewing and Rosenhain.<sup>3</sup> It is therefore important to realise that changes occur in metals both in the size of the grains and in that of the crystallites composing them, as the result of changes of temperature which may be far below the melting-point of the metal. Frequently, the granular structure of a metal or alloy is either visible to the unaided eye or under low powers of the microscope, provided the surface be suitably polished and etched. The student should refer to *The Metallographist*, vols. i. to vi., 1898–1903; the *Journals of the Iron and Steel Institute*; and

<sup>1</sup> H. E. Armstrong, *Min. Proc. Inst. C.E.*, vol. xciii. (1888), p. 112.

<sup>2</sup> Stead, *Journ. Iron and Steel Inst.*, 1898, ii. p. 137.

<sup>3</sup> *Proc. Roy. Soc., Bak. Lect.*, vol. cxciii. p. 353; also vol. cxcv. p. 279.



to the journals of similar institutions, for further particulars on this subject.

**Density.**—The density of a metal varies with the intimacy of the contact between the molecules. It is dependent, therefore, on the crystalline structure, and is influenced by the temperature of casting, by the rate of cooling, by the mechanical treatment, and by the purity of the metal. With the exception of bismuth, all pure metals are lighter when molten than when in the solid state. The density of a metal is augmented by wire-drawing, hammering, and any other physical method of treatment in which a compressing stress is employed. Mere traction, however, may diminish the density by tending to develop cavities in the metal. Pressure on all sides of a piece of metal increases its density. The density of standard gold, for example, by compression between dies is increased by 0·9, and cast discs of platinum, having a density of 21·21, may have the density increased to 21·46 by striking; whilst annealing such struck discs will again diminish their density. This shows that the compression is not permanent, and is solely due to the closing of pores. W. Spring<sup>1</sup> has even shown, by careful experiments on lead, tin, bismuth, antimony, cadmium, aluminium, and zinc, that a pressure of 20,000 atmospheres continued for many days is sufficient to effect the obliteration of all the pores. The specific gravities of the various metals are given in the table on p. 67. Lithium is the lightest metal, and osmium the heaviest, the specific gravity of the former being 0·54 and that of the latter 22·48.

So early as 1845, Joule<sup>2</sup> recognised the importance of determining the specific gravity of melted metals, seeing that "this condition would completely obviate the influence of cohesion, or that of any particular molecular arrangement." His method, which was essentially that afterwards adopted by Mallet<sup>3</sup> and by the author,<sup>4</sup> may be described as follows:—It consists in filling with molten metal a vessel, the capacity of which may be calculated for the particular temperature at which the molten metal is introduced. The weight of the metal when cold, divided by the weight of water which the expanded vessel is capable of holding, gives the fluid density of the molten metal. Subsequently the author<sup>5</sup> and T. Wrightson determined the fluid density of several metals by means of the oncosimeter as given below.

<sup>1</sup> *Bull. Soc. Chim. Paris*, vol. xxxix. (1883), p. 515; and Gray, *Proc. Roy. Soc.*, vol. liv. (1893), p. 28.

<sup>2</sup> Collected Papers, published by the Physical Society, vol. ii. p. 136.

<sup>3</sup> *Proc. Roy. Soc.*, vol. xxii. (1873), p. 366; and vol. xxiii. (1874), p. 209.

<sup>4</sup> *Ibid.*, vol. xxiii. (1874), p. 481.

<sup>5</sup> *Phil. Mag.*, vol. xi. (1881), p. 295; vol. xiii. (1882), p. 360.

	Specific Gravity of Solid.	Fluid Density.		Percentage of Change in Volume from Cold Solid to Liquid.	
		By Mallet's Method.	By Oncosimeter.		
Bismuth . . . .	9.82	10.039	10.055	Decrease of vol.	2.30
Copper . . . .	8.80	...	8.217	Increase of vol.	7.10
Lead . . . .	11.40	10.650	10.370	" "	9.93
Tin . . . .	7.50	6.974	7.025	" "	6.76
Zinc . . . .	7.20	6.550	6.480	" "	11.10
Silver . . . .	10.57	9.460	9.510	" "	11.20

The question of the fluid densities has also been investigated by Nies and Winkelmann,<sup>1</sup> who have adopted another method, determining the liquid density by observing the weights of blocks which just sink and just float. With regard to bismuth, C. Lüdeking<sup>2</sup> finds that this metal, like water, attains a maximum density just before becoming solid, the expansion at the moment of solidification being about 3 per cent. of the volume.

In 1895, Keep<sup>3</sup> described his apparatus for measuring the volume of a cast bar of metal or alloy, from the moment it begins to solidify until it reaches the atmospheric temperature, with which he studied the contraction of many solidifying metals and alloys. Prof. Turner<sup>4</sup> of Birmingham improved on Keep's apparatus, and also used a pyrometer for measuring the temperatures during solidification, contraction, and cooling.

From a large number of determinations, he found that the following four different types of curves could be obtained on plotting time and shrinkage:—

*Type 1.*—The contraction curve is uniform and there is no arrest in the decrease of volume as the metal cools. Copper, aluminium, antimony, lead, tin, and zinc yield curves of this type.

*Type 2.*—There is one point of retardation of the contraction, which may or may not lead to an actual expansion. White-iron, high carbon steel, and the copper-zinc alloys (many of which expand on solidification) belong to this class.

*Type 3.*—Two arrests in the rate of contraction are seen in this class, to which belongs non-phosphoric grey iron.

*Type 4.*—Three distinct arrests occur in this class, a characteristic curve being given by a very grey phosphoric iron.

From the curves given, Prof. Turner shows that during solidification there is no actual expansion with white iron, but with

<sup>1</sup> *Stitzungsber. der Acad. der Wissen. zu München*, 1881, p. 63.

<sup>2</sup> *Ann. Phys. Chem.*, vol. xxxiv. (1888), p. 21.

<sup>3</sup> *Journ. Iron and Steel Inst.*, 1895, ii. p. 227.

<sup>4</sup> *Journ. Iron and Steel Inst.*, 1906, i. p. 48.

grey irons there are two expansions, and with phosphoric grey irons there are three.

**Fracture.**—Fracture has long been used as a practical guide to the fitness of a metal, as in the refining of copper, the manufacture of steel, and in “grading” pig-iron. The influence of heat on the fracture of steel, although long recognised, was first dealt with systematically by Chernoff, and later and more fully by Brinell.<sup>1</sup> The appearance of the fractured surface of a metal depends partly on the nature of the metal and partly on the manner in which solidification occurred. Sudden cooling to a great extent prevents the formation of crystals, whilst slow cooling facilitates their development. Long-continued hammering and frequent vibrations will produce the latter result. Any condition that affects either the cohesion or the crystalline structure of a metal affects its fracture. Thus, lead broken when hot has a columnar structure; not so when broken cold.

The relation between the fracture and the internal structure of steels has received much attention; Seaton and Jude<sup>2</sup> examined the fractures produced by impact tests, and came to the conclusion that the line of fracture passed mostly through the ferrite portions, partly through the ferrite and pearlite junctions, and partly through the pearlite. Bannister<sup>3</sup> has shown that irregular and laminated fractures are frequently associated with “ghosts” or slag lines; and Rosenhain<sup>4</sup> has shown that in tensile fractures the break runs through the ferrite and pearlite almost indifferently, but in impact tests the break occurs in the ferrite for the most part, while bending fractures are of an intermediate character.

The ordinary mineralogical terms regarding colour and fracture are used in relation to metals. Practice, however, can alone enable the student accurately to describe these appearances.

**Malleability.**—This is the property of permanently extending in all directions, without rupture, by pressure produced by slow stress or by impact. Metals showing marked crystallisation, such as antimony and bismuth, are not malleable, and any circumstance that tends to produce crystallisation must affect the malleability. Thus in nearly all metals the malleability becomes impaired when they are subjected to rolling or long-continued hammering; but this property may be regained by annealing, which consists in raising the metal to a high temperature and allowing it to cool, either rapidly or slowly, usually the latter. At different temperatures metals behave in different ways; some are malleable when at a red heat, but not so when cold. These are defined as being *cold-short*.

<sup>1</sup> *Journ. Iron and Steel Inst.* (1886), p. 365; Howe's *Metallurgy of Steel*, p. 170; *Stahl und Eisen* (1885).

<sup>2</sup> *Proc. Inst. Mech. Eng.*, 1904, iv. p. 1135; *Engineer*, vol. xcvi. pp. 517 and 528, Nov. 18, 1904.

<sup>3</sup> *Journ. Iron and Steel Inst.*, 1906, i. p. 161.

<sup>4</sup> *Journ. Iron and Steel Inst.*, 1906, ii. p. 189.



Others are malleable when cold, but not when at a red heat. These are described as being *red-short*. Some metals are malleable at all temperatures, others are not malleable at all. Zinc is brittle when cold and when hot, but at a temperature of 150° it is malleable. The malleability of a metal depends largely upon its purity. Relative malleability is shown by the degree of thinness of the sheets producible by beating or rolling the metals without annealing.

**Ductility** is the property that enables metals to be drawn into wire. It generally decreases with an increase in the temperature of the wire at the time of drawing, but there is no regular ratio between the two. Iron is less ductile at 100°, and more ductile at 200° than it is at 0°. Malleable metals are also ductile, but they do not possess the two properties in the same order. Arranged according to their malleability, the more important metals follow this order:—(1) Gold; (2) Silver; (3) Copper; (4) Tin; (5) Platinum; (6) Lead; (7) Zinc; (8) Iron; (9) Nickel. The order of ductility, on the other hand, is (1) Gold; (2) Silver; (3) Platinum; (4) Iron; (5) Nickel; (6) Copper; (7) Zinc; (8) Tin; (9) Lead. The rate at which the traction is applied has great influence in testing malleability and ductility.

**Tenacity** is the property possessed by metals, in varying degrees, of resisting the separation of their molecules by the action of a tensile stress.

**Toughness** is the property of resisting the separation of the molecules after the limit of elasticity has been passed.

**Hardness** is the resistance offered by the molecules of a substance to their separation by the penetrating action of another substance or by abrasion. Great differences are observable between the hardness of the different metals, and many methods have been devised for its determination.

The results of the experiments of Bottone<sup>1</sup> gave valuable information. In these determinations the time necessary to produce a cut of definite depth when pressed against an iron disc revolving in a lathe, at definite speed, was taken as a measure of the hardness of the material. Prof. Turner<sup>2</sup> also investigated the hardness of metals and devised a sclerometer for the purpose of determining hardness.

This instrument has been modified by Keep, and consists of a diamond placed at the end of a well-balanced arm. By sliding a set of weights along the beam, a point is reached when the diamond makes a standard scratch. From the weights used and the position on the arm the relative hardness can be calculated. Brinell's<sup>3</sup> method of testing hardness is now largely used, and consists in producing an indentation in the material under ex-

<sup>1</sup> *Chemical News*, 1873, vol. xxvii. p. 215.

<sup>2</sup> *Proc. Birmingham Phil. Soc.*, vol. v., 1886, part ii.

<sup>3</sup> *Hallfasthetsprof*, by Wahlberg, Stockholm, 1901. *Journ. Iron and Steel Inst.*, 1901, i. p. 243; 1901, ii. p. 234.

amination by forcing into it a hardened steel ball. The maximum pressure applied, divided by the spherical area of the concavity (deduced from its diameter), gives as a quotient a number called the hardness number. The figures give a comparative determination of hardness only, and the following are the hardness numbers obtained for some metals and alloys:—

Rolled copper . . . .	74	Phosphor bronze . . . .	130
Silver . . . . .	59	Bell metal . . . . .	124
Antimony . . . . .	55	Brass . . . . .	63
Gold . . . . .	45	Phosphor tin . . . . .	19·7
Zinc . . . . .	46	Rose metal . . . . .	6·9
Aluminium . . . . .	38	Mild steel 0·1 C. . . . .	100
Tin . . . . .	14·5	Medium steel 0·45 C. . . .	200
Lead . . . . .	5·7	High carbon steel 1·25 C. .	300

A description of the machine used for obtaining the hardness number will be found under Testing Machines, page 33.

Prof. Unwin<sup>1</sup> also devised a method for testing hardness, similar in principle to Brinell's, in which a knife-edge was used for producing the indentation, instead of a ball, and the hardness number calculated from the load applied and depth of indentation produced.

Boynton<sup>2</sup> has recently used Jaggar's microsclerometer for the determination of the hardness of the different constituents of iron and steel. The principle of this instrument is as follows:—A diamond point of constant dimensions is rotated on the specimen at uniform rate, under uniform weight, to a uniform depth. The number of rotations necessary varies as the resistance of the material to abrasion by diamond. As a result of these determinations, the following figures were obtained:—

Constituent.	Present in	Average Hardness.	Ratio.
Ferrite	Electrolytic iron	460	1
"	" " (quenched)	990	2·15
"	Commercial wrought irons	686 to 1643	1·5 to 3·6
Pearlite	Series 0·13 to 1·52 per cent. carbon	842 to 4711	1·8 to 10·3
"	Series 0·35 to 0·86 per cent. carbon	1745 to 2150	3·8 to 4·2
Sorbite	Steels 0·48 and 0·58 per cent. carbon	2400 to 24,650	5·2 to 53·6
Troostite	Steel 0·58 per cent. carbon	40,560	88·2
Martensite	Series 0·2 to 1·52 per cent. carbon	17,896 to 120,330	38·9 to 261·6
Austenite	White cast iron 3·24 per cent. carbon	47,590	103·4
Cementite	White cast iron 3·24 per cent. carbon	125,480	272·8

<sup>1</sup> *Proc. Inst. Civil Engineers*, vol. cxxix., 1897.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1906, ii. p. 287.



**Brittleness** is the sudden interruption of molecular cohesion when the substance is subjected to the action of some extraneous force, such as a blow or a change of temperature. It is influenced by two distinct sets of conditions: one of these is the nature of the metal itself, such as chemical composition, structure, admixture with foreign matter, such as slag, blowholes filled with gas, etc.; and the other, the external conditions to which the metal is subjected, such as degree of stress, rate at which the stress is applied, shape of the test piece under examination, and temperature. Many cases of brittleness occur for which, at present, there is but imperfect explanation. Drop tests and falling weight tests are often the means of detecting material which, though satisfactorily fulfilling other conditions, yet is quite brittle under sudden shock. Fréminville<sup>1</sup> has studied the influence of vibration on the brittleness of bars of metal, and there has been much work done on brittleness in iron and steel; Stead<sup>2</sup> describes how soft steel may be rendered brittle by annealing; Law<sup>3</sup> shows that brittleness in steel sheets may result from high sulphur and phosphorus in the original ingots; and Charpy,<sup>4</sup> who has studied the effect of temperature on brittleness, states that in mild steels the minimum brittleness lies between 0° and 150° C., and the maximum brittleness between 250° and 500° C.

**Elasticity, Extensibility, and Strength of Metals.**—At first sight it might seem that testing the mechanical properties of metals is more within the province of the engineer than that of the metallurgist. The latter has, however, not only to extract metals from their ores, but also to fit them for use. He must therefore know what mechanical properties<sup>5</sup> are possessed by the more important metals and alloys, and be able to submit them to experimental tests, instead of merely trusting to statements recorded by others.

Elasticity is the power a body possesses of resuming its original form after the removal of an external force which has produced a change in that form. The point at which the elasticity and the applied stress exactly counterbalance each other is termed the **limit of elasticity**. If the applied stress were then removed, the material acted upon would resume its original form. If, however, the stress were increased, the change in form would become permanent, and **permanent set** would be produced. When considering, however, the stresses which a structure is

<sup>1</sup> *Revue de Métallurgie*, vol. iii. p. 61.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1898, ii. p. 137.

<sup>3</sup> *Journ. Iron and Steel Inst.*, 1906, i. p. 134.

<sup>4</sup> *Bulletin de la Société des Ingénieurs Civils*, 1906, p. 562.

<sup>5</sup> The more important works dealing with this subject are:—Kennedy, *Proc. Inst. C.E.*, vol. lxxxviii. (1887), p. 1; Unwin, *Testing of Materials of Construction*, 1889, Longmans; Lebasteur, *Les Métaux à l'Exposition Universelle*, 1878; J. Résal, *Constructions Métalliques: Élasticité et résistance des matériaux*, 1892; Martens, *Handbook of Testing Materials*, translated by Heming.

expected to bear without suffering "molecular fatigue," something considerably below the elastic limit is taken.

A very convenient term which expresses the condition of metals under stresses, when confined within the elastic limit, is that of "limit of proportionality," which has been given by French and German investigators to the point at which the strain ceases to be strictly proportional to the stress. Within the limit of elasticity, a uniform rod of metal lengthens or shortens equally under equal additions of stress. If this were the case beyond that limit, it is obvious that there would be some stress that would stretch the bar to twice its original length, or shorten it to zero. This stress, expressed in lbs. or tons for a bar of 1 inch square cross section, is termed the **modulus of elasticity**. As an illustration, let it be supposed that a bar of steel 1 inch square and 10 inches long is stretched by a force of 2240 lbs., and to have elongated under the action of this stress 0.00075 inch, the modulus of elasticity of this bar would be the force that would be required to elongate it by 10 inches, and this would be

$$0.00075 : 10 :: 2240 : x,$$

$x = 29.9 \times 10^6$  lbs. per square inch. Hence the modulus of elasticity is a stress that bears the same proportion to the original length of a uniform bar as the stress that will produce any given amount of strain bears to the length of this strain, the term **stress** meaning an equilibrating application of force to a body, and the term **strain** meaning any definite alteration of form or dimensions sustained by that body. The modulus of elasticity may thus be defined as being the number obtained by dividing the number expressing the stress by that expressing the strain that it produced. Unwin expresses this as follows:—

Let  $p$  be the stress reckoned on unit of area, and  $\lambda$  the extension or compression reckoned per unit of length.

Then, by Hooke's law,  $\frac{p}{\lambda} = E$ , a constant which is termed the coefficient of direct elasticity, or Young's modulus. It has the same value for tension and compression.

Thus, to take the above case of a sample of mild steel:—

Load applied, 2240 lbs. per square inch.

Extension produced, 0.00075 inch.

$$E = \frac{2240}{0.000075} = 29.9 \times 10^6 \text{ lbs. per square inch.}$$

Prof. Kennedy finds the **specific extension** to be a quantity most useful in works. This is the extension in thousandths of an inch on a length of 10 inches under a stress of 1000 lbs. per square inch. Its reciprocal, multiplied by 10 millions, is the modulus of elasticity in lbs. per square inch.

In measuring the strength of metals, it is necessary to determine—

1. The greatest **stress** the metal can sustain within the limit of elasticity.
2. The **strain** within the limit of elasticity.
3. The total extent of the **strain**, or alteration of form before rupture takes place.
4. The ultimate **tensile strength** or maximum stress the material can sustain without rupture.
5. The **reduction of area** at the point of fracture.

The limit of elasticity and the breaking stress are the points which have usually to be determined, and these alone will be considered here. For information as to torsional and compression tests, the student is referred to the works of Unwin and Kennedy.

In testing a piece of metal, the first point to be determined is the limit of elasticity. When a metal, such as iron or steel, is submitted to stress by pulling its ends in opposite directions, it stretches uniformly throughout its length. There is, however, in such a solid a limit in the application of the stress up to which the metal, if released, will return to its normal length. This point is the limit of elasticity. It is, however, certain that a very small application of load produces permanent deformation, so that the determination of the exact limit of elasticity will depend upon the delicacy of the instruments used for its measurement. It is safe to consider the limit of elasticity to be the point at which the stresses and strains cease to be exactly proportional. If the strains are plotted as abscissæ and the stresses as ordinates, points will be obtained on a curve giving the relation of stress and strain for the whole test. Up to the limit of elasticity, this curve is almost a straight line; but when that point is passed, the molecular arrangement of the metal breaks down, and, as Prof. Unwin expresses it, probably the breaking-down point (which is not to be confounded with the limit of elasticity<sup>1</sup>) is a kind of physical record of the condition of constraint in the bar at the moment of rolling or hammering. Fig. 1 is a curve obtained by an automatic recorder, showing the limit of elasticity, yield point, and breaking-down point of a specimen of open-hearth mild steel. It has been suggested by Osmond that in the case of iron or steel, any stress which produces a permanent deformation is attended by a rearrangement of the molecules of the metal. In support of this view, it may be mentioned that Carus Wilson<sup>2</sup> has examined this point of the stress-strain curve with much care, and shows that the peculiar bending of the

<sup>1</sup> See also Gautier, "Discussion on Testing Machine," *Journ. Iron and Steel Inst.*, vol. ii. (1888), p. 31.

<sup>2</sup> *Phil. Mag.*, vol. xxix. (1890), p. 200. See also the Sixth Report to the Alloys Committee, *Inst. Mech. Eng.*, 1904, p. 14.



curve indicates the condition of strain in a steel bar, since by gradually increased stress the steel may be converted from an elastic solid to a viscous fluid. He compares such curves (I to IV) fig. 2 for steel of different hardness with the stress-strain curves of a gas at different temperatures, there being strong probability that in

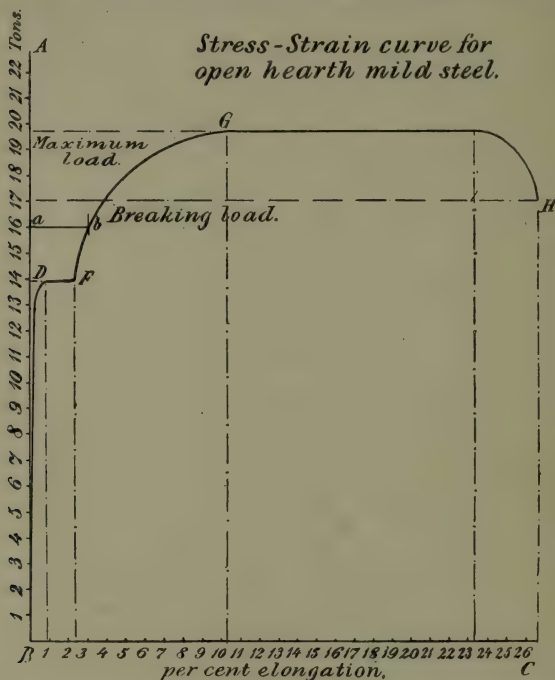


FIG. 1.—Elastic limit, 13.5 tons; D, yield point; F to G, curve of extension between yield point and maximum load; G, maximum load, 19.86 tons; H, breaking load, 17 tons. By dropping perpendiculars from any point in the curve, as at D, F, G, or H, to cut the base line, we get the percentage elongation for any particular load. Thus, at D it is rather under 1 per cent., at F just under 2.5 per cent., at G 10.25 per cent., and at H 26.65 per cent. Similarly, by drawing lines from any point in the curve parallel to the base line to cut the perpendicular load line, we can get the load on the specimen for any particular point in the curve.

both cases the apparent discontinuity, at AF, BE, and CD, is really a double inflection due to a change taking place piecemeal throughout the mass. Fig. 2 shows Carus Wilson's curve for the yield point of steel, and fig. 3 shows Andrew's curve exhibiting the passage of carbonic anhydride from the gaseous to the liquid state. Probably the increase in the breaking stress and diminution in

the elongation, which has been found to result from the application of long-continued stress to steel, is the result of the molecular change in the metal. It is also known that the prolonged application of a load to steel raises the elastic strength. This appears to afford additional evidence of molecular change. If the load is slowly applied, the stress-strain curve will be flatter than if it is applied rapidly.

Colonel Maitland<sup>1</sup> has conclusively shown that in the case of the unhardened steel used for the manufacture of guns, the

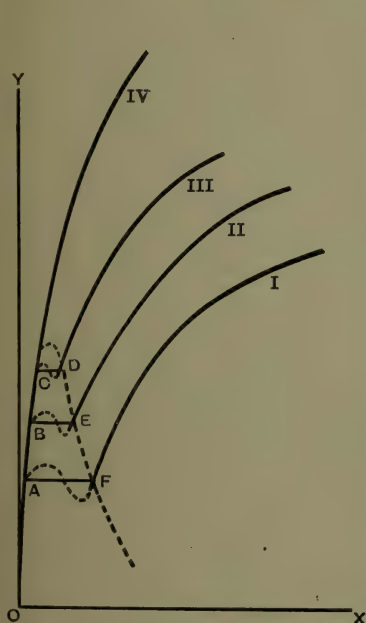


FIG. 2.



FIG. 3.

ultimate elongation is considerably increased by the rapid application of the load. The steel used showed a tenacity of 26 tons and an elongation of 27 per cent. on the length of 2 inches by the ordinary test, but when screwed into blocks, made to fall vertically in a slide, and arranged so that after a certain height of fall the top block was arrested by stops, and the specimen broken by the momentum of the lower block, the elongation increased to 47 per cent. On further increasing the rapidity of load by screwing the specimen into plugs fitting a strong tube, and exploding gun-cotton or gunpowder between

<sup>1</sup> *Min. Proc. Inst. C.E.*, vol. lxxxix. p. 120.



the plugs, thus driving them out in opposite directions, an elongation of 62 per cent. was obtained.

### Effect of High Temperatures on the Properties of Metals.

It is important to ascertain in what way the mechanical properties of metals are modified when they are submitted to tests while hot. André le Chatelier<sup>1</sup> has published some experiments in this direction in connection with a research on the influence of temperature on the mechanical properties of iron and steel. His results as regards a pure variety of ingot iron or mild steel containing 0.05 per cent. of carbon are given in the curves (fig. 4).

The effect of heat is to produce two modifications in the mechanical properties of iron and steel; there being a very noticeable reduction in elongation at a temperature of about 80°, and an

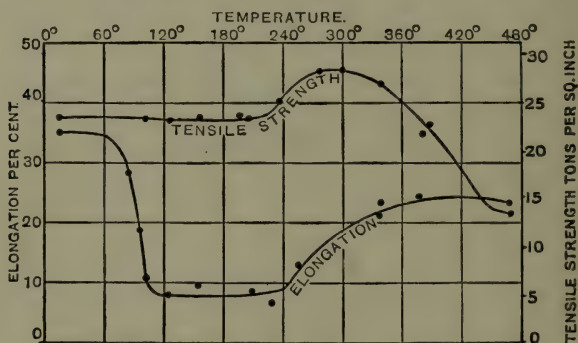


FIG. 4.

increase in the tensile strength at about 240°. These changes depend both on the temperature and on the speed with which the load is applied. The fragility of iron to shock is at its maximum at 300°, but it also possesses at this temperature a maximum resistance both to longitudinal stress and to extension if the load is slowly applied.

These results have been substantially confirmed by Ledebur<sup>2</sup> and others, but in many cases there is shown a slight decrease in tensile strength from -80° C. to a temperature of 60° C. to 100° C., after which a gradual increase is observed until about 320° C., when there is a gradual falling off again.

In the case of most ordinary metals, the tensile strength gradually diminishes as the temperature is raised, as is illustrated by the following table from the work of Baudrimont.<sup>3</sup>

<sup>1</sup> *Comptes Rendus*, vol. cix. (1889), p. 58.

<sup>2</sup> *Zeit. des Vereines deutscher Ingenieure*, vol. xl. p. 565.

<sup>3</sup> *Annales de Chimie et de Physique*, 1850.

## TENSILE STRENGTH IN POUNDS PER SQUARE INCH.

	At 0° C.	At 100° C.	At 200° C.
Gold . . . .	26,208	21,662	18,332
Platinum . . . .	32,144	27,440	24,528
Copper . . . .	35,728	31,136	26,000
Silver . . . .	40,320	33,040	26,432
Palladium . . . .	51,856	46,144	38,528

**Effect of Low Temperatures on the Properties of Metals.**

The effect of low temperatures on the mechanical properties of metals has received much attention of late years, one of the first investigators being Andrews, who published a paper in 1886 on the "Effect of Temperature on the Strength of Railway Axles."<sup>1</sup> The lowest temperature used in these experiments, however, was only  $-45^{\circ}\text{C}$ . As a general rule, the effect of very low temperatures on the common metals is to increase the tenacity, as measured by the breaking load, and to increase the hardness, as measured by the Brinell test.

Hadfield's experiments<sup>2</sup> showed that pure iron, soft and ductile at ordinary temperatures, became brittle, lost its ductility, and increased in hardness number from 88 to 263 on the Brinell scale, at liquid air temperatures, but on again reaching normal temperatures, became as soft and ductile as before.

Metallic nickel showed remarkable results when tested in liquid air, the tenacity increasing from 29 to 46 tons, the ductility from 43 to 51 per cent., and the hardness number from 100 to 150, and this fact probably explains why, in iron-nickel and iron-nickel-manganese alloys, the presence of nickel, provided there is a low percentage of carbon, prevents low temperatures, such as  $-150^{\circ}\text{C}$ . to  $-200^{\circ}\text{C}$ ., injuriously affecting the properties of the alloy. These alloys are dealt with on page 108. Metallic copper resembles nickel, the tenacity being increased, though not to the same extent, the ductility remaining the same and the hardness increasing from 77 to 90. Metallic manganese differs entirely from nickel and copper, being comparatively brittle at low temperatures. Aluminium shows increases in tenacity from 8 to 15 tons and ductility from 7 to 27 per cent. when tested in liquid air. Lastly, the effect of low temperatures on the ductility of lead and tin is most interesting, for although at ordinary temperatures they elongate about the same amount before breaking, tin breaks at  $-182^{\circ}\text{C}$ . without any extension,

<sup>1</sup> *Proc. Inst. Civil Eng.*, vol. lxxxvii., 1886-7, p. 340.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1905, l. p. 147.

while lead under similar conditions shows no change, stretching as much at  $-182^{\circ}\text{C.}$  as at  $15^{\circ}\text{C.}$

The following table gives the ultimate strength of a number of metals at ordinary temperatures:—

	Ultimate Strength. Lbs. per sq. in.		Ultimate Strength. Lbs per sq. in.
Copper, cast . . .	19,000	Lead, sheet . . .	3,200
„ annealed . . .	29,100	Tin . . . . .	3,400
„ hard drawn . . .	40,000	Gold, pure, cast . . .	15,680
Iron, cast, weak . .	13,400	„ drawn . . . . .	38,000
„ average . . . . .	16,500	Silver, drawn . . . .	40,000
„ strong . . . . .	27,300	Platinum . . . . .	35,000
Iron, wrought, plates	49,000	„ wire . . . . .	44,000
„ „ bars . . . . .	55,000	Aluminium, cast . .	10,976
Steel, mild . . . . .	50,000	„ bars . . . . .	16,128
„ medium . . . . .	88,000	„ drawn . . . . .	19,488
„ high carbon . . .	132,000	„ plates . . . . .	20,160

The influence of foreign elements on the tensile strength of metals is dealt with in Chapter III.

**Testing Machines.**—The elasticity and strength of metals are determined by the aid of testing machines, the more important of which are based on Kirkaldy's principle of applying the load by water pressure and measuring it by dead weight. In small machines, the hydraulic ram may be replaced by a screw and gear-

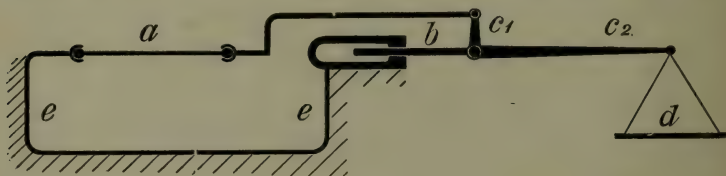


FIG. 5.

ing. Figs. 5 to 8, copied from Prof. Kennedy's admirable paper on engineering laboratories,<sup>1</sup> illustrate the principle of several types of testing machine, without showing the details of their construction. In the Werder machine (fig. 5), which has been largely used on the Continent, the test piece, *a*, is held at one end in the frame of the machine, *e*, and at the other pulled by means of the ram, *b*, from the short arm, *c*<sub>1</sub>, of a knee lever, to the long arm of which hangs a scale-pan, *d*, on which the pressure is balanced. The ratio of *c*<sub>2</sub> to *c*<sub>1</sub> is 500 : 10. The central fulcrum of the lever rests on the end of the ram, *b*, so that the whole

<sup>1</sup> *Min. Proc. Inst. C.E.*, vol. lxxxviii., 1887, p. 1.

measuring apparatus moves along as the piece extends and the ram moves out, the arm,  $c_2$ , being always kept horizontal by the aid of a spirit-level.

Wicksteed's machine<sup>1</sup> (fig. 6) is a vertical one with a single lever,  $c_1 c_2$ , placed horizontally on the top. A movable poise,  $m$ , measures the load, a downward pressure being applied to the

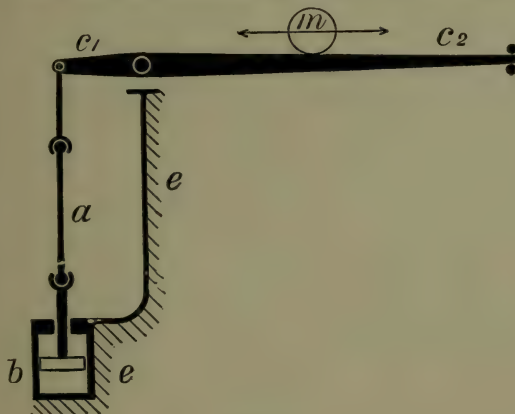


FIG. 6.

ram,  $b$ , by a screw or pump. The ratio of  $c_2$  to  $c_1$  is 50 : 1. In a 100-ton machine, the weight,  $m$ , is 1 ton, so that it balances a pull of 50 tons when at the end of  $c_2$ . To carry the load on to 100 tons,  $m$  is run back beyond the fulcrum, and a second weight of 1 ton is hung to the end of  $c_2$ . The poise weighs 1 ton, and is moved along the lever by a screw worked by power. Each 3

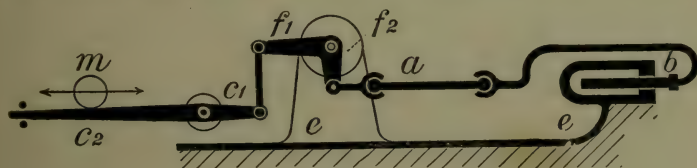


FIG. 7.

inches of movement of the poise adds 1 ton to the load on the test piece, whilst a vernier attached to the poise may be read, on a scale affixed to the lever, to one-hundredth of a ton.

Greenwood's machine (fig. 7) was formerly largely used in this country. It is a horizontal machine with two levers, a knee lever,  $f_2 f_1$  (5 : 1), and a steelyard,  $c_2 c_1$  (20 : 1), the total leverage being 100 : 1. The load is applied by the ram,  $b$ , and measured by the position of the poise,  $m$ , on the steelyard.

<sup>1</sup> *Inst. Mech. Eng. Proc.*, 1882, p. 384.



Gollner's machine (fig. 8) is a double lever vertical machine, working up to 20 tons. Both screw and ram may be provided with means for changing at once from one to the other.

A general sectional elevation of a modern Wicksteed machine, the principles of which have been described on page 27, is shown in fig. 9. This machine was built a few years ago for the Bradford Technical College by Messrs Buckton, and described by Mr G. F. Charnock in *Engineering*, from which article the drawing and description are taken. The machine is worked from an accumulator, G, and the ram, H,  $4\frac{1}{2}$  inches in diameter, is loaded to a pressure of 3000 lbs. per square inch, from a crosshead I, from which is suspended a load of about 24 tons of cast-iron

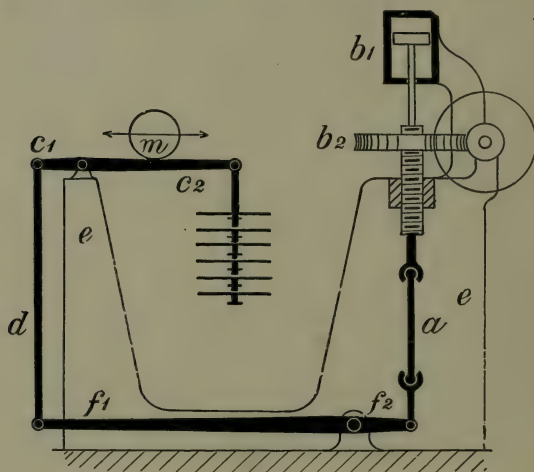


FIG. 8.

slabs I<sup>1</sup>. The accumulator is supplied by an automatic pump L.

The machine itself consists of a main standard, Q, a heavy box casting firmly secured to a massive stone foundation. The hydraulic straining cylinder, R, of 10 inches diameter and 12 inches stroke, is securely fixed in an inverted position to the base of the standard. The ram thus acts downwards, its crosshead, S, being connected by the two strong side screws, T, to the upper crosshead, U, which is guided by V slides on the face of the main standard, and in which is formed (1) the gripping-box for the lower end of a tension specimen Y, (2) a face for the upper end of a compression specimen when used for these tests; or (3) a pressure foot to apply the load at the centre of a beam specimen, when the machine is used for bending tests. The screws, T, are operated by worm gearing, worked by the handle, Z, and enable



the adjustment to any length of either tension or compression specimen up to 6 feet to be effected. The balance-weight, *a*, carried upon the end of spring levers, causes the return stroke

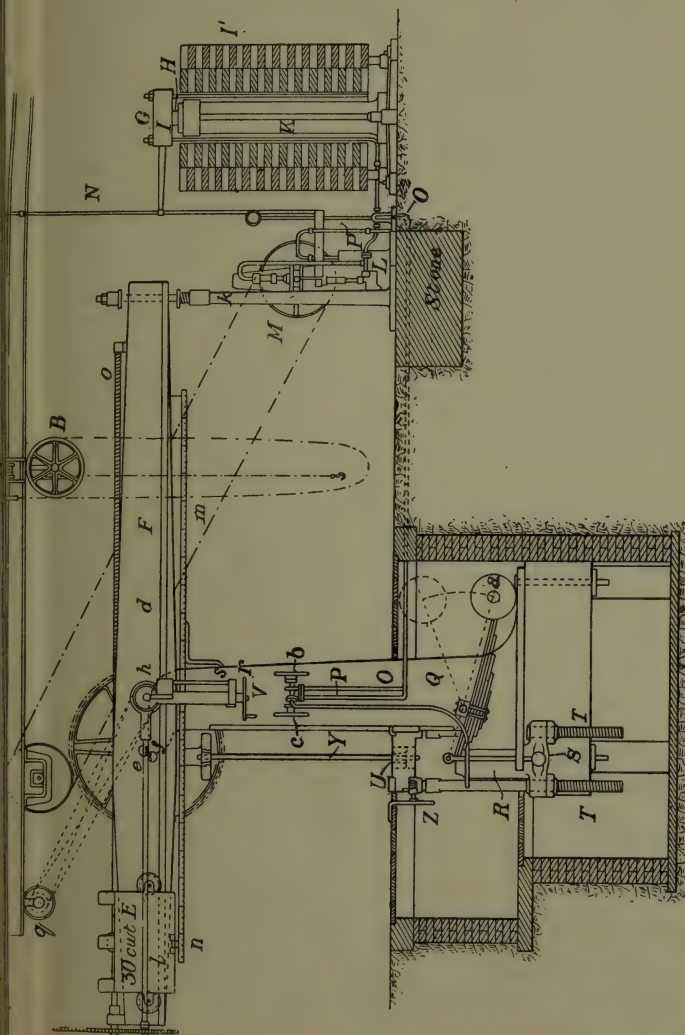


FIG. 9.—Wicksteed Testing Machine, Bradford College. A, small overhead traveller; B, 2-ton pulley blocks; E, travelling poise-weight; F, main lever; G, accumulator; H, accumulator ram; I, crosshead to ram carrying weights; K, cylinder of accumulator; L, pump for supplying accumulator; O, pressure pipe to ram accumulator; P, exhaust pipe to accumulator; Q, main cast-iron standard; R, hydraulic straining cylinder; S and U, crossheads attached to hydraulic ram; T, T, strong screws connecting crossheads S and U; Z, worm gearing for operating screws T; a, balance-weight; Y, specimen; b, pressure valve; c, exhaust valve; e, knife-edge fulcrum for F; f, graduated scale; m, vernier; n, screw; o, screw for moving poise-weight; q, counter shaft; r, hand-wheel for slow movement of E; s, reversing handle.

of the ram to be made after the conclusion of a test. The valve, *b*, admitting pressure from the accumulator, and the exhaust valve, *c*, for return to tank, are of the screw pattern worked by hand-wheels, and are easily adjustable to suit any speed of testing desired.

The main lever or steelyard, *F*, is double-ended, made of cast iron, and turns on a knife-edged main fulcrum, *e*, on the top of the main standard, and from a second knife-edge, *f*, hangs the upper shackle which carries the gripping-box for the upper end of a tension specimen, or from it may be suspended, by means of four strong rods, a table having a face for the bottom end of a compression specimen when the machine is used for these tests.

The knife-edges are of hardened steel, 20 inches long, and the fulcrum distance between them is 3 inches. The motion of the end of the lever is limited by stops, fitted with strong steel springs on the post, *k*. The travelling poise-weight, *E*, of 30 cwts., is of rectangular form, overhanging the sides of the main lever, so that its centre of gravity may be kept on the plane passing through the knife-edges. The graduated scale, *m*, is 200 inches long, reading 2 inches to the ton, and is carried upon brackets depending from the side of the lever. The vernier, *n*, which easily reads to  $\frac{1}{100}$  ton, is carried by the poise-weight, and its position is adjustable, so that when the lever has been put in balance it may be set to zero on the scale. The actual weight used for measuring the stress is double the weight of the poise, viz. 3 tons, and a leverage ratio of 33.3 to 1 is obtained.

The poise-weight is mounted on four rollers, which run on rails cast on the sides of the lever, and it is moved by a quick-threaded screw, *o*, which is rotated by spur wheels from a shaft fitted with Hooke's joint to allow of the motion of the lever, in connection with the reversing gear, *p*, driven by open and cross belts from the countershaft, *q*. A hand-wheel, *r*, is also provided for very slow motion or fine adjustment, and this, together with the reversing handle, *s*, and hydraulic valves, *b* and *c*, is placed within easy reach of the operator, who, without moving from his position, has the specimen in full sight, and can easily observe the movement of the lever. A small overhead traveller, *A*, is provided, actuated by hand-chains, fitted with a 2-ton pulley block, *B*, for moving large specimens and for lifting different parts of the machine.

In a testing machine it is extremely desirable to have some apparatus by the aid of which the stress-strain diagram of a piece of metal under test may be drawn automatically. Several types of apparatus of this kind have been devised. In the one by Wicksteed<sup>1</sup> (fig. 10), the motion of the pencil that indicates the load is derived from the pressure in the hydraulic press, and not from the weighing apparatus, a wire attached by clips to the specimen serving to rotate a recording drum by an amount proportional to the elongation. The pencil having an axial motion proportional to the load, and the drum a rotating motion proportional to the extension, a stress-strain diagram is described.

<sup>1</sup> *Inst. Mech. Eng. Proc.*, 1886, p. 27. For descriptions of American machines consult *Testing Machines: their History, Construction, and Use*, by A. V. Abbott, New York, 1884.

This apparatus has been improved in several particulars by Unwin.

*Details of Tests.*—The test bar may be of any convenient size, and either round or rectangular in section, but a circular bar is distinctly the best, as it can be more accurately gauged after fracture for the determination of the contraction of area. In the case of plates or bars, however, circular bars are generally impracticable, and a parallel strip of plate, as rolled, either shouldered down at each end or not, may be used.

The test piece having been carefully machined to the required shape, it is accurately gauged, preferably with a delicate screw micrometer, in at least three places along its length, and, if anything but a cylindrical bar, both the width and thickness taken; and from the mean of these measurements the area is calculated. A very

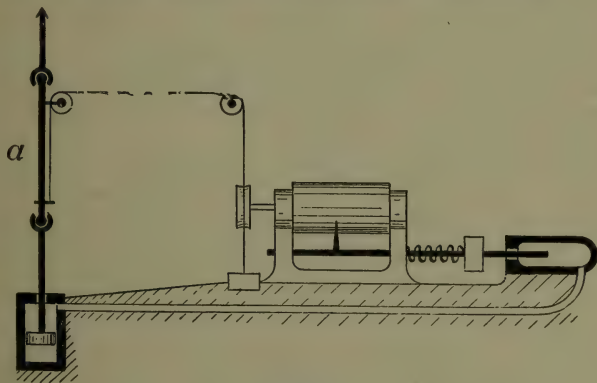


FIG. 10.

fine line is then drawn with a scribe along the surface of the bar, preferably along the centre of the wide side of a flat bar, and on this any distance, varying from 2 to 8 or 10 inches, according to the length on which it is desired to take the elongation, may be marked off by means of two very small punch-marks.

The test bar is then placed in the machine and the pressure applied until the beam lifts, when the weight is cautiously advanced along the beam to keep it floating in the horizontal position, measuring between the two stops on the top of the small standard *k* at the end of the beam (fig. 9). After the load reaches a certain point, the bar will suddenly elongate and, almost immediately, without any increment of load, the beam will drop on to the bottom stop: this is known as the yield point, a point just beyond the true elastic limit: the load at this point is read off, and if the pressure be continued, the beam will rise again and the weight will have to be advanced to keep the beam floating in the horizontal position between the stops until a point is



reached, when it suddenly drops again, indicating the maximum stress the bar will bear. To keep the beam floating, the travelling weight must be now rapidly run back to reduce the load until the rupture of the bar finally takes place, at a few tons less than the maximum stress, and this reading gives the "breaking load" in the *reduced sectional area*. Between the elastic limit and the maximum stress the bar stretches very rapidly; and when the maximum load is about reached, local reduction of area becomes very marked, and the sample of a ductile material rapidly "necks" down at the weakest point before final rupture takes place, as shown at A (fig. 11). If it is desired to determine the true elastic limit as distinct from the yield point, a pair of very fine dividers must be held in the two little distance marks on the test bar, and at the faintest sign of any stretching the load must be released to see if the bar returns to its original length. If no permanent stretch has taken place, slight increments of load are put on and taken off until a slight permanent set has taken place, which may be taken as marking the elastic limit. With careful work, fairly accurate results can be obtained by this method; but

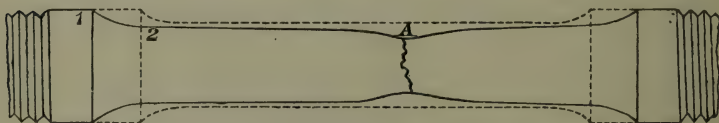


FIG. 11.—Sample of Steel before and after fracture.

if scientific accuracy is required, a special instrument known as an extensometer must be used, which, in the form designed by Ewing, is capable of measuring an extension of  $\frac{1}{250000}$  of an inch in a bar.

The bar having been broken, is removed from the machine, the reduced area in both halves at the point of fracture is carefully measured with the screw micrometer, and the reduction in area calculated from these measurements and expressed in percentages of contraction of the original area.

The elongation is determined by placing the two pieces of the broken bar carefully together and pressing the fractured ends close, and then measuring the length between the two distance marks. From the increase in length, in the original distance marked off, the percentage elongation on this given length is obtained. It is of great importance, in giving the percentage of elongation, to state the original length on which it is calculated; as, owing to the large local elongation which frequently takes place at the point of fracture, this, if distributed over 6 or 8 inches, would give a very different percentage result to what it would do if the length were only 2 or 3 inches.

For the determination of hardness by Brinell's method, the



most convenient arrangement is shown in fig. 12 whenever a compression testing machine is available. In this A and A' are compression blocks, there being placed on the lower one a small block, D, made of steel, with a cavity in the centre of the upper surface where the ball is to rest. The test specimen, B, is placed between the upper block, A, and the ball, C, and then the pressure is applied in the usual way until the required amount of loading is reached.

Fig. 13 shows a special Brinell machine designed for applying the pressure; it consists of four springs within a drum, with a screw-wheel arrangement, by means of which the loading operation is performed. The maximum pressure can then be read off on an

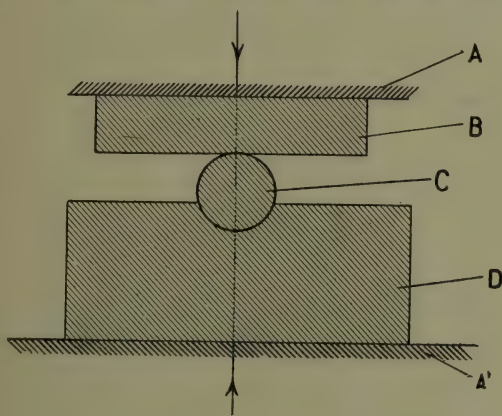


FIG. 12.—Brinell's method of Testing.

A A', compression blocks.  
B, test piece.

C, hardened steel ball.  
D, steel block.

indicator scale, empirically graduated, which is combined with the spring system.

**Impact Tests.**—During recent years very many methods have been devised by engineers for testing metals by impact, with a view of showing up weaknesses under sudden shocks or alternating stresses, which are not clearly indicated by the ordinary tensile tests.

The methods at present more or less used by engineers and metallurgists may be divided broadly into the following classes, according to the number and position of the notches and supports and method of applying the load.

(1) One notch in the centre of the bar: two supports: fracture effected by a series of blows of a falling weight. (*Seaton and Jude.*)

(2) One notch in the centre of the bar: two supports: fracture effected by one blow of a falling weight. (*Fremont.*)

(3) One notch, not necessarily in the centre: one support:

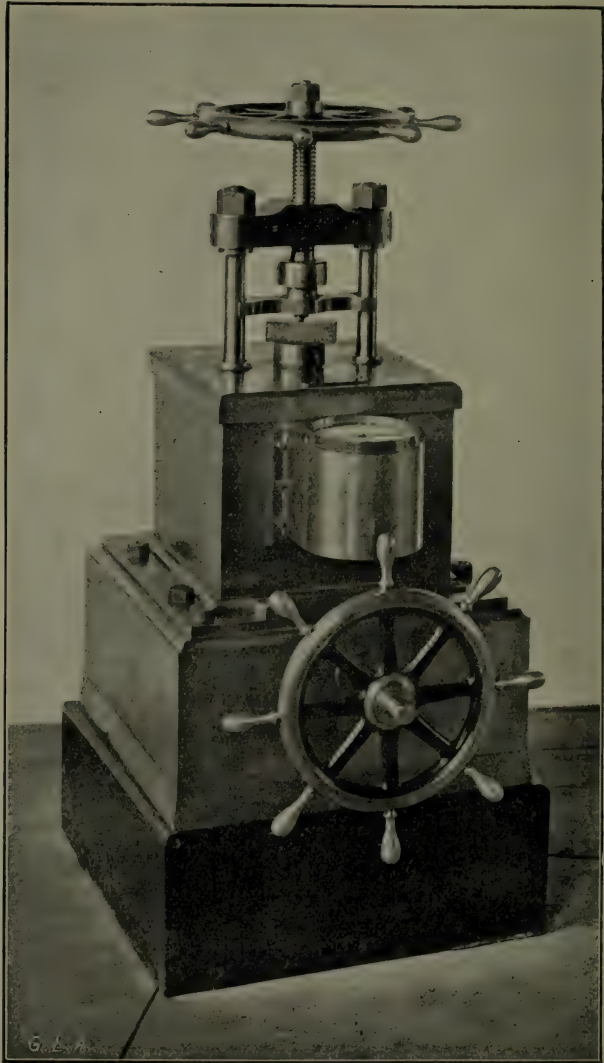


FIG. 13.

fracture effected by one blow on overhung portion from a falling pendulum or weight. *(Izod.)*

(4) Two opposite notches, not necessarily in the centre: one support: fracture effected by a series of blows of a falling weight on overhung portion. (Brinell.)

(5) Same as (4), but with an arrangement for reversing the bar after every blow. (Kirkaldy.)

The following is a description of the method of applying the test in the case of methods (1), (3), and (5):—

In the Seaton and Jude method a bar is taken, 4 in. long and  $\frac{1}{2}$  in. square in section, and a V notch  $\frac{1}{8}$  in. deep is cut in the centre of one side. The bar is supported on a bearing at each end, the notch being downwards, and is broken by a series of blows from a falling weight striking it on the centre. The weight and height of drop can be varied according to the metal under test. The energy absorbed in breaking the samples is calculated into foot-pounds. In the case of ductile steels requiring a number of blows, say seventy or more, the actual energy absorbed can be obtained to within one blow, that is, one-seventieth or so of the total energy, but in the case of brittle steels requiring only one to three blows, the error is still one blow, equal at least to one-third of the total, or even if one-half the last blow be taken as the breaking weight, the error would still be one-sixth of the total.

In the Izod method, a sample of the same shape and dimensions as used in the Seaton and Jude method with a V notch is used; this is supported at one end in a clip or vice and held vertically. Fracture is effected by one blow of a pendulum striking the overhung portion, and the residual energy in the pendulum is measured by the arc through which it swings after fracturing the sample. In this method an exact measure of the energy expended in fracturing the sample, within a very slight error, is obtained.

In the Kirkaldy method, the test piece is of the same dimensions as that used by Seaton and Jude, but instead of the V notch, it has two opposite circular grooves, each  $\frac{1}{8}$  in. deep at the centre of the bar. The test bar is supported in a suitable block or vice at one end and fractured by a series of blows from a falling weight on the overhung portion, but after every blow the entire block is turned over by a cam attachment, so that blows are delivered alternately on each side of the test bar. In this method, as in the Seaton and Jude, the force required to fracture the bar is calculated into foot pounds, and the degree of accuracy largely depends upon the number of blows which are required to produce fracture; owing, however, to the reversal after each blow, the number of blows required to produce fracture, even in very brittle steels, is comparatively large, and consequently the error is not very considerable, and in moderately ductile steels is inappreciable.

Various types of impact testing machines have been designed

**Acoustic properties.**—The sound emitted by metals when struck is greatly affected by the presence of impurities. Thus, in the case of lead, the presence of antimony tends to heighten the sound emitted. Owing, it is supposed, to the sliding of the crystal faces over one another, tin at ordinary temperatures, and zinc after heating to  $160^{\circ}$ , emit a sound or “cry” when bent.

**Properties common to Fluids and Solid Metals.**—Réaumur, so long ago as 1713, defined with singular clearness the conditions under which metals prove to be ductile. The relation between the behaviour of solid metals and fluids has long been recognised, not in the sense that atomic motion is common to solids and fluids, but from a wider view, for there is much experimental evidence as to the properties that are common to fluids and solid metals, the characteristics of which, at first sight, seem widely separated. A solid has a definite external form, which either does not change, or only changes with extreme slowness when left to itself, and in order to change this form rapidly it is necessary to submit it to a considerable stress. A liquid, on the other hand, can be said to have no form of its own, as it always assumes that of the containing vessel; the mobility of its particles is extreme, its resistance to penetration is very small, and its free surface is always a plane when the mass is left at rest. Then there is the colloid condition, which intervenes between the liquid and crystalline solid state, extending into both, and probably affecting all kinds of solid and liquid matter in a greater or less degree. The colloid or jelly-like body does present a certain amount of resistance to change of shape. Such a substance is well imitated by a sphere of thin india-rubber partly filled with water. Lastly, there is the gaseous condition of matter.

Metals are usually regarded as typical solids; it is easy, however, to trace the analogies of their behaviour under certain conditions with that of fluids. The transition from the liquid to the solid state is marked by the same phenomena in the case of many metals as are observed in certain fluids. For instance, metals on solidifying reject impurities, and exhibit the property of surfusion. This leads up to the relations between solid metals and fluids, and the following list shows the classes in which the properties common to fluids and solid metals may be grouped:—

1. Flow under pressure.
2. Changes due to compression.
3. Absorption of liquids.
4. Surface tension.
5. Absorption of gases.
6. Diffusion.
7. Vaporisation.

Water, on passing from the liquid to the solid state, undergoes a partial purification, the ice first formed being sensibly more



free from colouring matter or suspended particles than the water from which it separates.

Many metals, on freezing, similarly eject impurities. In the case of alloys, saturated solutions of one metal in another appear to be formed, and excess of metal ejected, a fact which was studied with much care by Dr Guthrie. The prominent facts are perhaps best illustrated by reference to a solidified mixture of copper, antimony, and lead. The results of some experiments conducted, in the laboratory of the Royal School of Mines, by Dr E. J. Ball<sup>1</sup> show that when a molten mixture of these metals is solidified, a definite atomic alloy of copper and antimony, which possesses a beautiful violet tint, first forms, and, after saturating itself with lead up to a certain point, ejects the rest of the lead, driving it to the centre of the mass so as to form a sharp line of demarcation between the outer violet circle and the grey centre. It thus presents a direct analogy to the comparatively colourless ice which first forms from coloured water. There is yet another remarkable analogy between the freezing of certain fluids and the solidification of some metals. Water may, as is well known, be cooled down to  $-8^{\circ}$  C. without solidification, but agitation immediately determines the formation of ice, and, at the same time, a thermometer plunged in the water rises to zero. Faraday stated,<sup>2</sup> in 1858, that fused acetic acid, sulphur, phosphorus, many metals, and many solutions would exhibit the same effect. Tin also may be cooled to several degrees below its solidifying point without actually freezing; and Dr Van Riemsdijk<sup>3</sup> of Utrecht has observed that a globule of gold or silver in a fused state will pass below its solidifying point without actually solidifying, but the slightest touch with a metallic point will cause the metal to solidify, and the consequent release of its latent heat of fusion is sufficient to raise the globule to the melting-point again, as is indicated by a brilliant glow which the button emits.

The result of Raoult's investigations on the lowering of the freezing-point of solutions led him to the conclusion that one molecular proportion of any substance dissolved in 100 molecular proportions of any solvent whatever lowers the freezing-point of that solvent  $0.62^{\circ}$  C. This had not been tested in the case of solutions of metals in metals until Heycock and Neville<sup>4</sup> began an elaborate investigation of the subject. Their research dealt first with the lowering of the freezing-points of various metals by the addition to them of certain other metals, and, second, with the molecular weights of metals when in solution. The results of their experiments when compared with the empirical laws of Coppey and Raoult may be briefly stated as follows:—

<sup>1</sup> *Journ. Chem. Soc.*, vol. liii. (1888), p. 167.

<sup>2</sup> *Experimental Researches in Chemistry and Physics*, p. 379.

<sup>3</sup> *Ann. de Chim. et de Phys.*, t. xx. (1880), p. 66.

<sup>4</sup> *Journ. Chem. Soc.*, vol. lv. (1889), p. 666; vol. lvii. (1890), pp. 376 and 656.

They are in accordance with the law "that for moderate concentration the fall in the freezing-point is proportional to the weight of the dissolved substance present in a constant weight of solvent." By making the assumption that the molecule of zinc or of mercury is monatomic when in solution in tin, they confirm the second law, "That when the falls produced in the same solvent by different dissolved substances are compared, it is found that a molecular weight of a dissolved substance produces the same fall whatever the substance is." But the third law, which states "That if a constant number of molecular weights of the solvent be taken, then the fall is independent of the nature of the solvent," they found to be probably incorrect, and theoretical considerations indeed would lead us to expect this.

In a research of much interest, Ramsay<sup>1</sup> has determined the molecular weight of a number of metals by Raoult's vapour pressure method—that is, he ascertained the depression of the vapour pressure of the solvent produced by a known weight of dissolved substance, and he finds that although sodium behaves irregularly, yet "it would appear legitimate to infer that in solution, as a rule, the atom of a metal is identical with its molecule, as the physical properties of those metals which have been vaporised would lead us to suppose."

Now to pass to solid metals. It is the common experience that a counterfeit shilling, consisting principally of lead, does not "ring" when thrown on a wooden surface. In 1726 Louis Lemery observed that lead is, under certain conditions, almost as sonorous as bell-metal.<sup>2</sup> He communicated the fact to Réaumur, who, being much struck by it, investigated the conditions under which lead becomes sonorous, and submitted the results to the French Academy.<sup>3</sup> He pointed out that, in describing a body which is not sonorous, it is usual to say that it is as "dull as lead," an expression which has become proverbial. Nevertheless, he adds, under certain conditions, lead has a property both novel and remarkable, for it emits surprisingly sharp notes when struck with another piece of lead. He showed that it was necessary that the lead should be formed by casting into a segment of a sphere—that is, mushroom-shaped. The lead must be free from prominences, and must be neatly trimmed. The effect is less marked if the lead be very pure than if ordinary commercial lead be used, but it is only a question of degree. Réaumur showed that the sonorous lead might be rendered dull by hammering it. His remarks have been overlooked in late years. He was led to the belief that in cast lead there must be an arrangement of the

<sup>1</sup> *Journ. Chem. Soc.*, vol. lv. (1889), p. 521. See also Tammann, *Zeit. für physikal. Chemie*, 1889, p. 441.

<sup>2</sup> Hoefler, *Histoire de la Chimie*, ii. p. 383.

<sup>3</sup> *Histoire de l'Académie Royale des Sciences, Année 1726* [vol. for 1728, p. 243].

interior of the mass which the hammer cannot impart, because lead fashioned by hammering into the same form as the sonorous cast mass is dull, and, more important still, he held that the fibrous and granular structure of the lead is modified in a manner which makes it probable that the sound is due to the shape of the grains and to the "way in which they touch each other"; further, the blows of the hammer not only change the arrangement of the fibres, but they alter the shape of the grains; "the round grains are rendered flat, they are compelled to elongate and fill the interstitial spaces which previously existed between them. The particles are no longer free to vibrate; hence the lead is dull." These facts acquire additional interest if they are compared with the observations in Prof. Osborne Reynolds' paper on "Dilatancy in Granular Matter." Réaumur's description shows that he fully appreciated the theoretical importance of the kind of facts depending on the transfer of metallic matter from one position to another, which we now consider to be characteristic of the "flow" of metals; at any rate, Lemery's experiment may be made the starting-point of the remarks which follow.

A solid may be very brittle, and may yet, if time be given to it, flow from one point to another. A stick of sealing-wax, or even of glass, supported at its ends, in a few weeks bends at the ordinary atmospheric temperature, although at any given point of its flow it would have been easy to snap it with a slight application of force. A tuning-fork may be made from pitch, which will nevertheless subside into a shapeless mass at the ordinary temperature. A much thinner strip of pure lead of the same breadth as the sealing-wax also bends at the ordinary temperature with its own weight, the ends being supported. Lord Kelvin has, however, pointed out that a gold wire, sustaining half the weight which would actually break it, would probably not rupture in a thousand or even a million years—that is to say, there would be no "flow" ending in disruption; if, however, force be suitably applied, metals will flow readily. First, examine the case of a metal under force applied so as to compel it to flow through a hole, as it points to the analogy of an ordinary viscous fluid. If a vessel (1, fig. 14) provided with a cylindrical hole in its base be filled with lead, the lead will, at the ordinary pressure, remain there, but if extra pressure be applied the lead will prove by its behaviour that it is really a viscous solid, as it flows readily through the orifice; the end of the jet is rounded, and, as has been shown by the beautiful researches of the late M. Tresca of Paris,<sup>1</sup> all the molecules which compose the original block place

<sup>1</sup> These researches extend through a long series of memoirs; those relating to the flow of metals are well summarised in the *Proc. Inst. Mech. Engineers*, 1867, p. 114, and in the Report of the Science Conferences held in connection with the Loan Collection of Scientific Apparatus (Physics and Mechanics), London, 1876, p. 252.



themselves in the jet absolutely as the molecules of a flowing jet of a viscous fluid would. If the metal has a constant "head," as it would be termed in the case of water—that is, if the vessel be kept filled with solid lead up to a certain level—then there will be a continuous stream, the length depending on the constancy with which the "head" and the pressure are maintained. If, on the other hand, the "head" is diminished so that nearly all the solid lead has been allowed to flow away (2, fig. 14), there is a folding of the jet, and vertical corrugations, exactly such as would characterise the end of the flow of certain other viscous fluids, and finally the jet forms a distinct funnel-shaped tube concentric with the jet. It is also seen that, when the formation of these cavities takes place, the jet is no longer equal to the full diameter of the orifice, as shown in 2, fig. 14, the formation of the con-

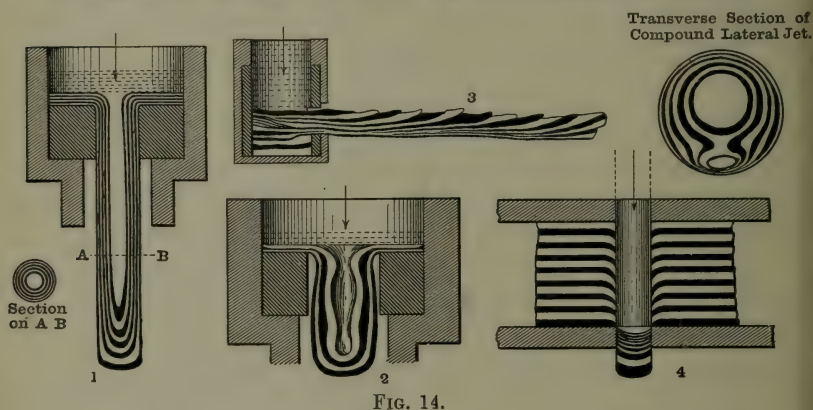


FIG. 14.

tracted vein is manifest, and the new analogy is thus obtained between the flow of solids and of liquids.

In punching a disc from a solid plate of metal supported by a die plate (4, fig. 14), as in the operation of coining, the portion cut out proves to be thinner than the plate from which it has been removed. Since the density of a metal is not increased by pressure except by the obliteration of pores, as has already been stated, it follows that the metal must have flowed in a plastic state laterally from the disc into the plate, the remaining metal becoming so thin that its resistance to shearing is less than the pressure on the punch.

In 3, fig. 14, the effect is shown of a compound jet of lead flowing through a lateral orifice in a cylindrical vessel.

In the case of planing surfaces of metals by cutting tools, similar effects may be traced, and it is interesting to compare the flow of metal in 4, fig. 14, which represents the penetration of a cutting tool through a plate of metal, with the flow of metal



under the action of a tool used for planing (fig. 15). In this case the lines of flow are made evident by the deformation of lines traced vertically on the side of the block of metal submitted to the tool. The shifting of the material and the connection of the lines, F, in the shaving, with those, E, of the original block, will be evident from the diagram. Every artificer knows how complicated in form the shavings may be, and varied problems relating to their production have been studied by M. Tresca.<sup>1</sup>

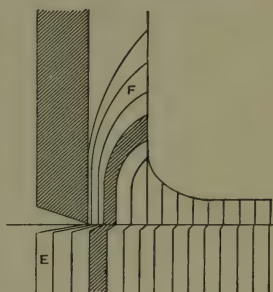


FIG. 15.

The application of this fact, that solid metals flow like viscous fluids, is of great importance in industry, and the production of complicated forms by forging or by rolling iron and steel and other metals entirely depends on the flow of the metal when suitably guided by the artificer. The lines of flow in iron may be well shown by polishing a surface of the metal, and by submitting it to the action of a solution of mercuric chloride, which etches the



FIG. 16.

surface, or better, to the slow action of chromic acid solution, the result in either case being, that any difference in the hardness of the metal, or in the chemical composition, or want of continuity, caused by the presence of traces of entangled slag, reveals the manner in which the metal has flowed. The sketches illustrate the direction of flow in the following cases. Fig. 16 is a

<sup>1</sup> *Mémoires de l'Académie des Sciences*, vol. xxvii., No. 1, 1880.

section of a forged cross-head, and figs. 17 and 18 are sections of rails.

The experiments of M. Tresca were not made on "steel"; it is therefore interesting to compare the etched section of the old rail, fig. 17, the result of the complicated welding of puddled iron, with a basic-Bessemer rail, rolled from steel which has been cast, and which is therefore free from entangled slag. Fig. 18 represents a section of such a rail.

A very striking illustration of the importance of the flow of metals, when used in construction, is afforded by some observations of Sir B. Baker in a paper on the Forth Bridge.<sup>1</sup> He says: "If the thing were practicable, what I should choose as the material for the compression members of a bridge would be 34-to 37-ton steel, which had previously been squeezed endwise, in the direction of the stress, to a pressure of about 45 tons per



FIG. 17.



FIG. 18.

square inch, the steel plates being held in suitable frames to prevent distortion." He adds: "My experiments have proved that 37-ton steel so treated will carry as a column as much load as 70-ton steel in the state in which it leaves the rolls—that is to say, not previously pressed endwise. . . . At least one-half of the 42,000 tons of steel in the Forth Bridge is in compression, and the same proportion holds good in most bridges, so the importance of gaining an increased resistance of 60 per cent. without any sacrifice in the facility of working, and safety, belonging to a highly ductile material can hardly be exaggerated."

The very ancient mechanical art of striking coin is wholly dependent on the flow of metals. There is a popular belief that the impression imparted to discs of metal during coinage is merely the result of a permanent compression of the metal of which the disc is made. Striking a coin, however, presents a case of moulding a plastic metal, and of the true flow of metal,

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1885, p. 497.

under pressure, into the sunken portions of the die. A medal struck from a series of discs will serve to show, when the discs are separated, the way the metal flows into the deepest portion of the die. If the alloy used be too hard, or if the thickness of the metal required to flow be insufficient, the impression will always be defective, no matter how many blows may be given by the press.

If one side of the coin be ground away, so as to leave a flat surface, and if the disc be then struck between plain polished dies surrounded by a steel collar, so as to prevent the escape of the metal, the impression on the disc will be driven through the thickness of the metal, and will then appear on both sides. In industrial art the property of flow of metals is very important. The "spinning" of articles in pewter is a familiar instance.

The production of complicated forms, like a jelly mould, from a single sheet of copper, under the combined drawing and compressing action of the hammer, is a still more remarkable case.

The flow of metals is illustrated very curiously in one phase of Japanese art metal-work, to which reference will be made subsequently.

The flow of metals when submitted to compression has hitherto been alone considered, but the effect of traction has also been examined, for when a viscous metal such as iron or soft steel is submitted to stress by pulling its ends in opposite directions, it stretches uniformly throughout its length, and the metal truly flows when the yield point is reached. The limit of elasticity of a solid body marks the moment at which the body begins to permanently stretch, under the influence of the longitudinal stress to which it is submitted. There are many materials which do not stretch sensibly when their limit of elasticity is reached; in very hard steel, for instance, the breaking-point and the limit of elasticity practically coincide. Further, it must be observed that every minute variation in composition is sufficient to change the property of a body, and to cause what was a viscous body to break close to the limit of elasticity.

The particles of a metallic powder left to itself at the ordinary atmospheric pressure will not unite; by "augmenting the number of points of contact in a powder" the result may be very different. The powders of metals may weld into blocks, as will subsequently be described, and it will be seen that experiments on the compression of finely divided metals afford important evidence as to the relation between solid metals and fluids. Faraday discovered, in 1850, that two fragments of ice pressed against each other will unite, their tendency to union being considerable when the fragments are near their melting-point. Ice owes its movement in glaciers, not to viscosity, but to regelation, and the union of fragments of ice under compression is also due to regelation. The facts which have been appealed to, and the theories which have been formed,



respecting the regelation of ice, are well known ; it may, however, be observed that bismuth, like ice, expands on solidifying ; and though Faraday failed to establish the existence of a property similar to regelation in bismuth, Wrightson has satisfied himself, by experimental evidence, that regelation exists in bismuth. In explaining Spring's results (p. 74) there is this difficulty : the union of the particles of the metals cannot, in all cases, be due to viscosity, because viscous bodies are always capable of being stretched, and we find the welding taking place between the compressed powders of bodies, such as zinc and bismuth, which, when submitted to traction, will not stretch. Spring therefore asks, "Is it possible that regelation may have something to do with the union of the powders?" and he urges, "Is it safe to conclude that regelation is peculiar to ice alone?" "It is difficult to believe," he adds, "that in the large number of substances which Nature presents to us, but one exists possessing a property of which we can find only minute traces in other bodies. The sum of our chemical and physical knowledge is against such a belief, and therefore the phenomenon of regelation may be pronounced in ice without being absolutely wanting in other bodies. To ascertain whether this is so, it is necessary to submit other bodies to the conditions under which the phenomenon can be produced." "What," he asks, "are these conditions?" and he answers, "The pressure supported by the body, a certain degree of temperature, and time."

Both Helmholtz and Tyndall have shown that when the pressure is weak the regelation of ice is effected slowly. Spring points out that nitrate of sodium and phosphate of sodium, in powder, left to themselves in bottles, become coherent ; and if the coherence in these and other chemical compounds is but weak, it is simply because the points of contact between the particles of powder are but few. If, on the other hand, metallic or other powder be submitted to strong compression, the spaces between the fragments become filled with the *débris* of the crushed particles, and a solid block is the result. Finally, it may be urged that this union of powders of solid metals under the influence of pressure—that is to say, the close proximation of the particles—can be compared to the liquefaction of gases by pressure. At the first view this comparison may appear rash or strained, but it is not so if the views of Clausius on the nature of gases and liquids be accepted. In a gas the molecules are free, but if by pressure at a suitable temperature the molecules are brought within the limit of their mutual attraction, the gas may be liquefied, and, under suitable thermal conditions, solidified. The mechanical pulverisation of a metal merely detaches groups of molecules from other groups, because the mechanical treatment is imperfect, but the analogy between a solid and a gas has, in this sense, been established ; filing "coarsely gasifies" the mass, but pressure solidifies it.

It is possible that in some of the compressed metallic blocks



the particles are not actually united by the pressure, which may, nevertheless, develop the kind of "mutual attraction" contemplated by Lord Kelvin as existing between two pieces of matter at distances of less than 10 micromillimetres.

Another analogy between metals and fluids is presented by the power which certain solid metals possess of taking up fluids, sometimes with a rapidity which suggests the miscibility of ordinary fluid substances. In reference to this, an interesting paper was published, so long ago as 1713, by the Dutch chemist Homberg,<sup>1</sup> "On Substances which Penetrate and which Pass Through Metals without Melting Them." He enumerates several substances which will pass through the pores of metals without disturbing the particles, and he points out that mercury penetrates metals without destroying them. The rapidity with which mercury will pass through tin is remarkable. A bar 1 inch wide and  $\frac{1}{2}$  inch thick will be penetrated by mercury in thirty seconds, so that it breaks readily, although before the addition of the mercury the bar would bend double without any sign of fracture.

In relation to surface tension, there is an interesting property belonging to a hard drawn rod or thick wire of 13-carat gold, the gold being alloyed with silver and copper in the following proportions:—

Gold . . . . .	54.17
Copper . . . . .	33.33
Silver . . . . .	12.50
	<hr/>
	100.00

If such a rod be touched with a solution of chloride of iron or certain other soluble chlorides, it will in a short time, varying from a few seconds to some minutes, break away, the fracture rapidly extending for a distance of some inches.

**Occlusion of Gases.**—With reference to the absorption of gases by metals, Sainte Claire-Deville and Troost discovered that hydrogen would pass through a plate of platinum, prepared from the fused metal or through iron, at a red heat; and it was well known that molten silver had the power of absorbing many times its own volume of oxygen. In Deville's experiments a new kind of porosity was imagined, more minute than that of graphite and earthenware, an intermolecular porosity due entirely to dilatation. Graham<sup>2</sup> showed that when gas penetrates the substance of the metal there is previous absorption and possibly liquefaction of the gas. Since his time it has been abundantly recognised that the presence of an element which is capable of reappearing with the elastic tension of a gas must materially affect the

<sup>1</sup> *Mém. de l'Acad. Royale des Sciences*, 1713 (vol. for 1739, p. 306).

<sup>2</sup> *Proc. Roy. Soc.*, vol. xvi. p. 422; vol. xvii. p. 212 and p. 500. *Trans. Roy. Soc.*, 1886, pp. 399–439.

mechanical properties of a metal. Palladium is known to possess the power of occluding gas—hydrogen—in the most marked degree. By slow cooling from a red heat in an atmosphere of hydrogen, palladium foil or wire occludes no less than 900 volumes of hydrogen. Similarly, gold is found to occlude, that is, *retain when solid*, 0.48 of its volume of hydrogen and 0.2 of its volume of nitrogen, silver occludes 0.7 of its volume of oxygen, and wrought copper occludes 0.306 volume of hydrogen.

It is, however, in relation to the metallurgy of iron that the occlusion of gases is of importance. It is well known that at the conclusion of the Bessemer process, oxygen from the air blown through the metal becomes intimately associated with the iron; and Müller<sup>1</sup> has given strong evidence in support of the view that gases are dissolved in iron. Hydrogen is usually present in iron, chiefly as gas, sometimes as ammonia,<sup>2</sup> and in certain cases probably in some non-gaseous state. It does not appear to be in strong chemical combination, as it can easily be expelled. This may happen on solidification of the metal, by heating *in vacuo*, or by the action of a drill, which appears to release entangled or loosely-held hydrogen. The escape of gas can be prevented by increasing the pressure during solidification, and by the addition, before solidification, of silicon, manganese, or aluminium. The hydrogen probably remains in the cold iron after it is solidified. Cailletet<sup>3</sup> extracted from electrolytic iron, in which the metal probably exists in a distinct molecular form, nearly 250 times its volume of hydrogen by heating *in vacuo*. Graham proved that carbonic oxide is dissolved by iron, and that that gas probably plays an important part during the conversion of iron into steel in the ordinary process of cementation. It is certain that the presence of silicon and manganese appears to enable the iron to retain carbonic oxide, as well as hydrogen and nitrogen, in solution.

In an appendix to his paper on the "Determination of the Allotropic Changes of Iron by the Measurement of the Variations in Electric Resistance," Boudouard<sup>4</sup> gave some analyses of the gases given off on heating different varieties of steel *in vacuo*. Among the gases so examined were carbonic oxide, hydrogen, nitrogen, and oxygen, which he found in carbon and some chrome steels, whilst from steels containing tungsten, manganese, and nickel he obtained no gas.

Oxygen not only exists in steel as occluded gas, but in the form of oxide; and Law<sup>5</sup> has recently shown the great influence

<sup>1</sup> *Iron*, 1883, vol. xxi. p. 115, and vol. xxii. 244; 1884, xxiii. p. 161.

<sup>2</sup> Recognised by many observers; notably by Regnard, *Comptes Rendus*, vol. lxxxiv. (1877), p. 260.

<sup>3</sup> *Comptes Rendus*, vol. lxxx. (1875), p. 319.

<sup>4</sup> *Journ. Iron and Steel Institute*, 1903, i. p. 371.

<sup>5</sup> *Journ. Iron and Steel Inst.*, 1907, ii. p. 98.

this has on the physical properties of the steel, especially in the case of tin plates. He described the appearance of oxide of iron under the microscope as consisting of minute black specks distributed throughout the mass of the metal. These can only be seen if the specimen has received a perfect polish and requires a magnification of at least 1000 diameters; besides these oxide patches, a certain amount of oxide exists in solution in the iron.

In a number of determinations, the oxygen was found to vary from 0.021 per cent. in good steels to 0.046 in bad steels; these quantities seem extremely small, but it must be remembered that 0.046 per cent. of oxygen corresponds to 0.2 per cent. of ferrous oxide, which is an appreciable amount of impurity for steels. It is interesting to note that oxide of iron, when present in steel, has a powerful influence on its liability to corrosion, increasing this to a considerable extent.

**The Diffusion of Metals.**—The results of a research on the diffusion of certain liquid and solid metals in each other, which occupied the attention of the author from time to time, were the subject of the annual "Bakerian Lecture"<sup>1</sup> for 1896. Until this investigation was undertaken very little attention had been devoted to the consideration of the molecular movements which enable two or more molten metals to mix spontaneously and form a truly homogeneous fluid mass. A single example of such spontaneous mixing, borrowed from Mint practice, may be sufficient. In preparing the alloy of gold and copper used for coinage, some 1100 ozs. of gold and 100 ozs. of copper are melted at a time in a crucible, and the results of assays on pieces of metal which represent the first and last portions poured from the crucible need not differ by more than  $\frac{1}{100000}$ th part. Such a fluid mass of gold owes its singular uniformity in composition not only to the mechanical stirring by which the blending of the gold and copper is roughly effected, but also to the fact that the metals dissolved in each other become spread or diffused uniformly by a spontaneous process. It is well known that such molecular movement occurs when salts are dissolved in water, and the rate at which various salts dissolve and diffuse in water has been accurately measured by Graham.

Very little has, however, been done as regards the measurement or even the consideration of the molecular movements in fluid metals, and the absence of direct evidence upon the point is probably explained by the want of a sufficiently accurate experimental method. An eminent physicist, Ostwald, has stated, with reference to the diffusion of salts, that "to make accurate experiments in diffusion is one of the most difficult problems in practical physics," and the difficulties are obviously increased when working with metals at high temperatures. It is, moreover, well known

<sup>1</sup> *Phil. Trans.*, vol. clxxxvii. (1896), A. p. 383.



that the rate of saline diffusion is greatly augmented by a comparatively small increase of temperature, a fact which suggests that the thermal measurements in diffusion experiments must be accurately made.

The want of a ready method for the measurement of comparatively high temperatures, which led to the abandonment of the author's earlier work, is overcome by the recording pyrometer, and the use of thermo-junctions in connection with this instrument rendered it possible to measure and record the temperature at which diffusion occurred.

The tubes containing the lead in which the diffusion was to take place were arranged in a little furnace of special construction. In the earlier experiments the tubes were placed in a bath of molten lead, but this was abandoned in favour of an air bath with double walls, which could be heated above the melting-point of lead and readily maintained at definite temperatures. The drawing (fig. 19) shows the general arrangement. The diffusion tubes are closed at the base, and two of such tubes are shown at  $TT'$ , placed in a cylinder of iron,  $I$ , 3 inches in diameter and 7 inches high. The sectional plan shows six of the diffusion tubes arranged symmetrically in this iron cylinder, which is enclosed in a second cylinder of thick copper,  $C$ ,  $4\frac{1}{4}$  inches in diameter and  $8\frac{1}{4}$  inches high. The lower half of this copper vessel is surrounded with a layer of asbestos cloth,  $A$ . There is a lid composed of two discs of copper,  $DD'$ , with asbestos between them. If, for any special reason,  $U$  tubes should be employed, one open end of each tube might communicate with a hole in the double lid, and the metals the diffusion of which is to be studied could be introduced through this hole. They fall by gravity to the base of the  $U$  tube, and then rise by diffusion up to its opposite limb.

The heating is effected by a series of clay gas-burners,  $BB'$ , mounted on a ring,  $RR'$ , the burners surrounding the upper portion of the copper cylinder. Investing cases of fireclay,  $GG'G''G'''$ , and a lid of clay,  $H$ , complete the construction of the furnace.

It is, of course, a matter of great importance to obtain a gas supply of constant volume, and this has been effected by means of a regulator; a delicate gauge is also provided, and by its aid any variation in the pressure of the gas is indicated.

The absence of a trustworthy method for the measurement of the temperature would have rendered it impossible to conduct these experiments, but by the aid of thermo-junctions such measurement can readily be effected. These thermo-junctions,  $JJ'J''$ , are shown in fig. 19, and it was only necessary to connect them in turn with the recording pyrometer in order to obtain a continuous record of the temperature at three positions in the air bath, but as regards each of the three positions this record is



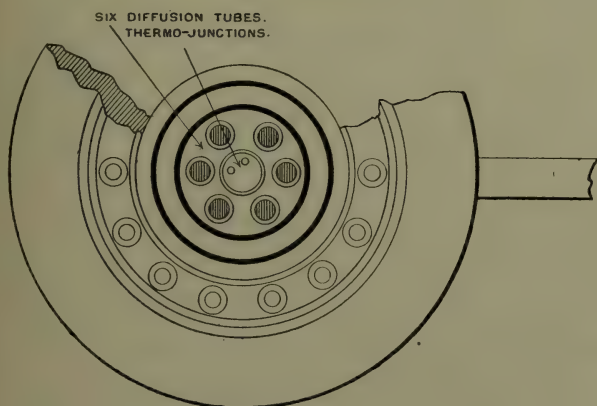
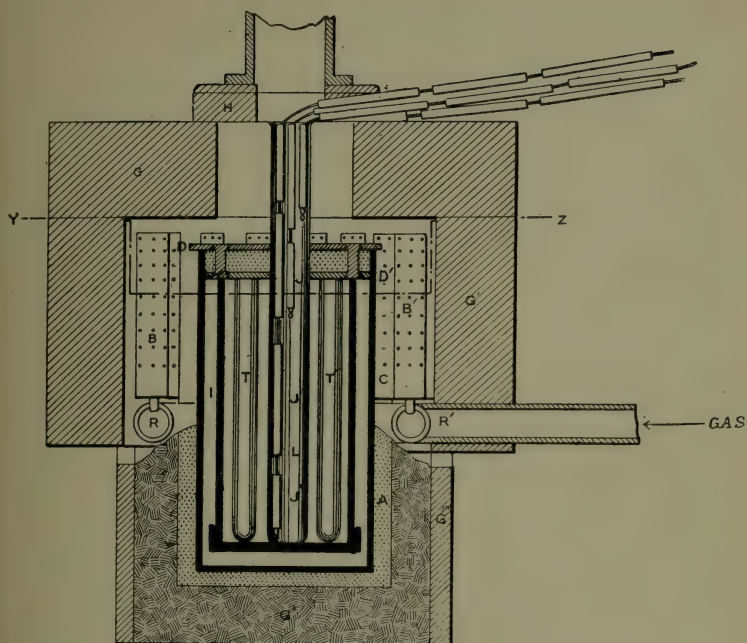


FIG. 19.

intermittent, and the indications afforded by each individual thermo-junction form a dotted, not a continuous line. The intermittence is, however, very rapid, and the result is three clear and distinct time-temperature records, which enable any variation in temperature to be readily detected and measured. The records, which are very numerous, show that while there was no rapid variation of temperature, there was, however, a gradual fall in temperature from the beginning to the end of the experiment, and this is due to the fact that the burners became slightly obstructed by the products of the combustion of the gas, and in later experiments a thermostat was employed. The occasional slight adjustment of the gas-taps by hand, in accordance with the indications of the thermo-junctions, rendered it possible to maintain a very constant temperature. Much care was taken to prove that the method of inserting the thermo-junctions down a central tube really indicated the mean differences of temperature between the upper, middle, and lower portions of the bath, and it was shown that there was no object in continuing the use of a lead bath, which was first adopted, as it greatly complicated the manipulation.

The amount of metal diffusing in a given time was ascertained by allowing the lead in the tubes to solidify; the solid metal was then cut into sections, and the amount of metal in the respective sections determined by analysis.

The movement in linear diffusion is expressed, in accordance with Fick's law, by the differential equation

$$\frac{dv}{dt} = k \frac{d^2v}{dx^2}.$$

In this equation  $x$  represents distance in the direction in which diffusion takes place,  $v$  is the degree of concentration of the diffusing metal, and  $t$  is the time;  $k$  is the diffusion constant, that is, the number which expresses the quantity of the metal in grammes diffusing through unit area (1 sq. cm.) in unit time (one day) when unit difference of concentration (in grammes per c.c.) is maintained between the two sides of a layer 1 cm. thick. The experiments have shown that metals diffuse in one another just as salts do in water, and the results were ultimately calculated by the aid of tables prepared by Stefan for the calculation of Graham's experiments on the diffusion of salts:

The necessary precautions to be observed and the corrections to be made are described at length in the author's paper, to which reference has been made.

The results of the diffusion during twenty-four hours of platinum and gold in fluid lead, contained in tubes placed side by side, and heated to a temperature of 500°, are represented in the accompanying diagram (fig. 20). The columns A B represent the columns

of fluid lead  $2\frac{3}{4}$  in. long and  $\frac{3}{16}$  in. wide. The spheres represent the relative sizes of the buttons of gold and of platinum extracted from the several sections, shown by horizontal lines, into which the columns of lead were divided after the metal had been allowed to solidify. With regard to the curves which are marked respectively gold and platinum, the vertical ordinate represents the *distance* in which diffusion takes place, and the horizontal ordinate, concentration. Each of the metals, gold and platinum, which diffused into the fluid column of lead, occupied, in the form of an alloy with lead, the length  $ad$  of the tube, and in both cases the initial concentration of the

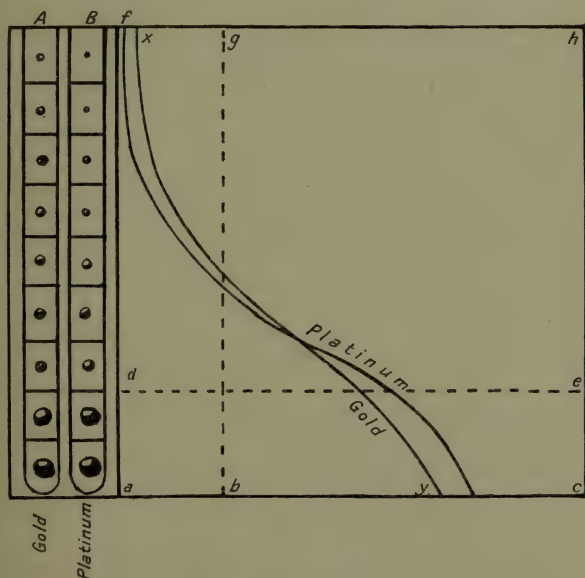


FIG. 20.

alloy denoted by  $ac$ , from which diffusion proceeded, was the same, so that the area  $aced$  represents the total amount of gold or platinum employed in the experiments, the whole quantity of either metal being initially below the line  $de$ . The final state of complete diffusion would be represented by the area  $abgf$ , which is the same as  $aced$ , since the quantity of gold or platinum remains unaltered. In the same manner, the area  $ayxf$  would represent the distribution of the gold at the end of the experiment, and consequently, in experiments which have lasted for equal times, the nearer the curve approximates to the line  $bg$ , the more rapid is the diffusion of the metal it represents.

The results for a few metals are given in the following table.

Diffusing Metal.	Solvent.	Temperature.	<i>k</i> in square centimetres.	
			Per diem.	Per second.
Gold	Lead	492°	3·00	3·47 × 10 <sup>-5</sup>
"	"	492	3·07	3·55 "
Platinum	"	492	1·69	1·96 "
"	"	492	1·69	1·96 "
Gold	"	555	3·19	3·69 "
"	Bismuth	555	4·52	5·23 "
"	Tin	555	4·65	5·38 "
Silver	"	555	4·14	4·79 "
Lead	"	555	3·18	3·68 "
Gold	Lead	550	3·18	3·69 "
Rhodium	"	550	3·03	3·51 "

In order to afford a term of comparison, it may be stated that the diffusivity of chloride of sodium in water at 18° is 1·04.

In these experiments on the diffusion in liquid metals, the prevailing conditions in the ordinary diffusion of liquids were maintained, that is, there was always present a large excess of the solvent metal which is supposed to exert but little chemical action on the diffusing substance. It must also be remembered that Van't Hoff<sup>1</sup> has made it highly probable that the osmotic pressure of substances existing in a *solid* solution is analogous to that in liquid solutions and obeys the same laws, and it is also probable that the behaviour of a solid mixture, like that of a liquid mixture, would be greatly simplified if the solid solution were very dilute.

Nernst expresses the hope that it may be possible to measure by indirect methods the osmotic pressure of substances existing in solid solutions. The following experiments may sustain this hope by affording measurements of the results of osmotic pressure in masses of *solid metals* at the ordinary atmospheric pressure, and at a temperature at which it has hitherto been scarcely possible to detect diffusion in them.

The experiments constitute, so far as the author is aware, the first attempt to actually measure the diffusivity of one solid metal in another. It must be borne in mind that the union of two clean surfaces of metal, and even the interpenetration of two metals to a slight depth below the surfaces, does not necessarily depend on diffusion alone, as the metals become united in a great measure by viscous flow. The nature of welding demands

<sup>1</sup> *Zeitschr. Phys. Chem.*, vol. v., 1890, p. 322.



investigation, but the union of metals by welding is effected most energetically when the metals are in the colloidal condition, in which true diffusion is least marked. It may be observed that discs of gold and lead, pressed together at the ordinary temperature for three months, were found to have welded together more perfectly than two similar discs kept in contact at 100° for six weeks, although at least ten times more metal had interdiffused in the latter case than in the former.

For a complete description of the experiments and results, reference should be made to the original paper.<sup>1</sup> It may be sufficient to point out that a curve indicating the diffusion of gold in solid lead would have the same general form as the curve shown above recording the diffusion of gold in fluid lead (fig. 20), but the time required for gold to penetrate to different points of the cylinder would be far greater in the case of solid lead than in the fluid metal. This will be evident by referring to the following figures, which give the value of  $k$ —that is, the diffusivity of gold in solid lead—at various temperatures, from 251° to 100° C., and these figures show that the diffusivity of gold in solid lead at 100° is only  $\frac{1}{100000}$ th of that in fluid lead at a temperature of 550°.

Diffusivity of gold in fluid lead at	550°	.	.	3·19
" " solid "	251°	.	.	0·03
" " " "	200°	.	.	0·007
" " " "	165°	.	.	0·004
" " " "	100°	.	.	0·00002

These experiments naturally suggested the inquiry whether gold will permeate lead at the ordinary temperature, or must a certain amount of viscosity be given to it by the application of a moderate heat? In order to test this matter, pure lead cylinders, each with a smooth surface at its base, were clamped into close contact with the clean surface of a disc of gold, and so maintained undisturbed at a temperature of about 18° C. for four years. Successive slices were then cut at right angles to the axis of the cylinders and assayed for gold. These assays showed that the portion in contact with the gold had absorbed a quantity equivalent to 1 oz. 6 dwts. of gold per ton of lead, while the slice 6 mm. above the gold<sup>2</sup> had absorbed a quantity equivalent to 1½ dwts. per ton.

**“Kernel Roasting.”**—There has long been a prevalent belief that diffusion can take place in solids, and the practice in conducting certain important industrial processes supports this view. One of these processes, which is of comparatively ancient date, has certainly been employed since 1692 at Agordo, and its results are as follows:—When lumps of cupriferous iron pyrites are

<sup>1</sup> *Bakerian Lecture*, 1896.

<sup>2</sup> *Proc. Roy. Soc.*, lxvii., 1900, p. 101.

subjected to very gradual roasting with access of air, the copper becomes concentrated as a "kernel" of nearly pure sulphide of copper in the centre of a mass of ferric oxide, while, at the same time, the silver originally present in the ore travels outwards and forms a glistening shell on the exterior. These complicated changes must be effected in the solid by a movement allied to diffusion. The kernel often consists of nearly pure  $\text{Cu}_2\text{S}$  which melts at  $1135^\circ \text{C}$ ., and kernels are formed in ore roasted at lower temperatures in the roasting heaps or kilns.

**Cementation Processes.**—Of all the processes which depend on the diffusion of solids, probably the most interesting is the truly venerable one by which silver may be recovered from either plates or globules of solid gold by "cementation," the name being derived from the "cement" or compound in which the plates were heated. Its nature was indicated by Pliny, and the manipulation it involved was minutely described by Geber in the eighth century, as well as by many of the early metallurgists; Savot,<sup>1</sup> for instance, pointed out in the early part of the seventeenth century that "cementation" will deprive gold of the silver it contains, "however small" the amount of the latter metal may be, so that it will be evident that the elimination of the silver from the centre of a mass of solid gold must also be effected by an intermolecular movement allied to diffusion. The evidence, however, is not conclusive, because gaseous chlorine intervenes, and may even play an important part in the penetration of the solid metal.

In another ancient "cementation" process, the conversion of strongly heated but still solid iron into steel is effected by the passage of solid carbon into the interior of the mass of iron, and the explanations which have from time to time been given of the process form a voluminous literature. Le Play considered cementation, which is really a slow creeping action of one solid into another, to be "an unexplained and mysterious operation," and he attributed the transmission of the carbon to the centre of the iron solely to the action of gaseous carbonic oxide. Gay-Lussac<sup>2</sup> confessed that a study of the process shook his faith "in the belief generally attributed to the ancient chemists that *corpora non agunt nisi soluta*," for it is certain, he adds, "that all bodies, solid, liquid, or aeriform, act upon each other, but, of the three states of bodies, the solid state is the least favourable to the exercise of chemical affinity."

In 1881 M. A. Colson<sup>3</sup> communicated a paper to the Académie des Sciences, in which he showed that when iron is heated in carbon there is a mutual interpenetration of carbon and iron at so low a temperature as  $250^\circ$ . The interpenetration of solids, as distinguished from the diffusion of two metals in each other,

<sup>1</sup> *Discours sur les Médailles antiques*, 1627, p. 76.

<sup>2</sup> *Ann. de Chim. et de Phys.*, vol. xvii., 1846, p. 221.

<sup>3</sup> *Comptes Rendus*, vol. xciii., 1881, p. 1074; vol. xciv., 1882, p. 26.

has received attention from many experimenters, of whose work brief mention will only be given, as the subject of this part of the book is the diffusion of solid metals. Colson pointed out that pure silver diffuses as chloride in dry chloride of sodium, and he states that calcium passes into platinum when the latter is heated in lime, and that silica diffuses through carbon and yields its silicon to platinum. The permeation of strongly heated porcelain by carbon has been demonstrated by Marsden, Violle, and other experimenters. Spring,<sup>1</sup> in 1885, showed that solid barium sulphate and sodium carbonate react on each other until an equilibrium is established.

Any lingering doubt as to whether gas need necessarily intervene in the cementation of iron was removed by an experiment of the author's,<sup>2</sup> in 1889, which showed that pure iron may be carburised by diamond *in vacuo*, at a temperature far below the melting-point of iron, and under conditions which absolutely preclude the presence or influence of occluded gas.

The rate of diffusion of carbon in iron was studied by the author<sup>3</sup> in 1896, and since then much work has been published on this subject by Guillet, Charpy, Bauer, Arnold and M<sup>r</sup>William and others. Guillet,<sup>4</sup> in his work, investigated the influence of original carbon content, temperature, duration of experiment, and kind of carbonaceous matter or cements used. He found that the penetration of carbon into iron or steel was the same after eight hours' treatment at a temperature of 1000° in two cases, in which the original metal contained .055 per cent. and .5 per cent. of carbon respectively. He obtained the following depths of penetration of carbon on heating iron at 1000° in carbonaceous matter—

$\frac{1}{2}$ hour	.	.	.	.	.	.	.5 mm.
1 "	.	.	.	.	.	.	.8 "
2 hours	.	.	.	.	.	.	1.0 "
4 "	.	.	.	.	.	.	1.3 "
6 "	.	.	.	.	.	.	2.0 "
8 "	.	.	.	.	.	.	3.0 "

—and the following figures illustrate the influence of temperature, the specimens being heated for eight hours in each case:—

At 800°	.	.	.	.	.	.	.5 mm.
850	.	.	.	.	.	.	1.0 "
900	.	.	.	.	.	.	1.6 "
925	.	.	.	.	.	.	2.0 "
950	.	.	.	.	.	.	2.8 "
1000	.	.	.	.	.	.	4.2 "
1050	.	.	.	.	.	.	5.2 "

<sup>1</sup> *Bull. de l'Acad. Roy. de Belgique*, vol. x., 1885, p. 204.

<sup>2</sup> *Nature*, vol. xli., 1889, p. 14.

<sup>3</sup> *Journ. Iron and Steel Inst.*, 1896, i. p. 139.

<sup>4</sup> *Mémoires de la Société des Ingénieurs Civils de France*, 1904, No. 1, p. 177.



With regard to special steels, he divides them into two groups:—(1) Steels in which the cementation process is either reduced or actually prevented by increasing quantities of other constituents, such as nickel, titanium, silicon, aluminium. (2) Steels in which the other constituents assist the cementation process, such as manganese, chromium, tungsten, and molybdenum. Arnold and M'William<sup>1</sup> studied the diffusion of various elements in iron, by using cylinders of nearly pure iron, 3 inches long and 0·7 of an inch in diameter, bored through with a hole 0·35 inch in diameter; bars of iron containing about 1·5 per cent. of the elements, the diffusive power of which was about to be determined, were turned dead true to the exact diameter of the hole in the jacket. The latter was heated to about 150° C. to expand the hole a little, and the core was driven home, so that, on cooling, the bright surfaces of the jacket and core were in close contact. A hole for the insertion of the thermo-couple was made in the core, and the compound bar was introduced into a porcelain tube and heated *in vacuo* in a tube furnace. After heating *in vacuo* for ten hours at a temperature ranging between 950° C. and 1050° C., portions were turned off the jacket and analysed to ascertain the amount of the element contained in the core that had passed into the jacket. The following table shows the diffusive power of elements in iron.

Element.	Original Percentage in Jacket.	Original Percentage in Core.	Percentage in the $\frac{1}{8}$ th inch of Jacket adjacent to the Core after Experiment.	Percentage diffused in Ten Hours.
Carbon . . .	0·05	1·78	0·55	0·50
Sulphur . . .	0·02	0·97	0·12	0·10
Phosphorus . .	0·015	1·36	0·11	0·095
Nickel . . .	0·00	1·51	0·11	0·11
Manganese . .	0·05	1·29	0·04	none
Silicon . . .	0·027	1·94	0·028	"
Chromium . .	0·00	1·10	0·00	"
Aluminium . .	0·02	1·85	0·02	"
Tungsten . . .	0·00	1·41	0·00	"
Arsenic . . .	0·02	1·57	0·012	"
Copper . . .	trace	1·81	trace	"

This solid diffusion of metals is closely connected with the formation of alloys by cementation, a subject which will now be considered.

**Formation of Alloys by Cementation.**—The fact that alloys can be formed by the union of two metals at a temperature below

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1899, i. p. 85.



the melting-point of the more fusible of the two has long been known to metallurgists, and perhaps the most striking fact in the more modern history of the subject was recorded in 1820 by Faraday and Stodart,<sup>1</sup> who, in the course of an investigation on the alloys of iron with other metals, noted their failure to produce certain alloys by "cementation," but consider it "remarkable," in the case of platinum, that it will unite with steel at a temperature at which the steel itself is not affected. They also show that solid steel and platinum, in the form of bundles of wires, may be welded together "with the same facility as could be done with iron or steel," and they observe that on etching the surface of the welded mass by an acid "the iron appeared to be alloyed with the platinum." Their interest in this singular fact led them to promise some direct experiments on "this apparent alloy by cementation," that is, by the interpenetration of solids. Since this time there have been many more or less isolated observations bearing on the subject, and brief reference may be made to the more important of them in chronological order. In 1877 Chernoff<sup>2</sup> showed that if two surfaces of iron of the same nature be placed in intimate contact and heated to about 650° they will unite. In 1882 Spring<sup>3</sup> made his remarkable experiments on the formation of alloys by strongly compressing their constituent metals at the ordinary temperature, while, in 1885, O. Lehmann<sup>4</sup> suggested, and in 1888 Hallock<sup>5</sup> demonstrated, that compression is not necessary, as alloys might be formed by placing carefully cleaned pieces of two constituent metals in juxtaposition and heating them to the melting-point of the alloy to be formed, which was, in some cases, 150° below the melting-point of the more fusible of the two metals. In 1889 Coffin showed—and the author has repeatedly verified the accuracy of his experiment—that if the freshly fractured surfaces of a steel rod 9·5 mm. square be placed together and heated to below redness, they will unite so firmly that it is difficult to pull them apart by hand. The steel was highly carburised, and the diffusion of a carbide of iron probably played an important part in effecting the union. There must have been molecular interpenetration in this case, though the steel was at least 1000° below its melting-point. In 1894 Spring<sup>6</sup> proved that if the carefully surfaced ends of cylinders of two metals were strongly pressed together and maintained for eight hours at temperatures which varied from 180° to 400°, interpenetration would

<sup>1</sup> *Quarterly Journal of Science*, vol. ix., 1820, p. 319.

<sup>2</sup> *Revue Universelle des Mines*, vol. i., 1877, p. 411.

<sup>3</sup> *Ber. der Deutsch. Chem. Gesell.*, xv., 1882, p. 595.

<sup>4</sup> *Wied. Ann.*, xxiv., 1885, p. 1.

<sup>5</sup> Communicated to Phil. Soc. of Washington, Feb. 18, 1888; *Zeitschr. Phys. Chem.*, ii., 1888, p. 6, or *Chem. News*, vol. lxiii., 1891, p. 17.

<sup>6</sup> *Bull. de l'Acad. Royale de Belgique*, vol. xxviii., 1894, p. 23.

take place, true alloys being formed at the junction of the two metals.

In these experiments, which are of great interest, the temperatures at which the cylinders were maintained were below the melting-point of the more fusible of the two metals. Care appears to have been taken to avoid heating them up to the melting-point of the *eutectic* alloy, though it was in some cases close to it. The necessity for this precaution will be obvious, as the union of the two compressed cylinders might easily be effected by the fusion of an eutectic alloy with a relatively low melting-point.

**Diffusion of Amalgams in Mercury.**—A number of experiments have been made on the diffusion at ordinary temperatures of gold and other metals in mercury, from which it was found that the diffusivity of gold in mercury at 11° C. is 0·72 sq. centim. per day, the diffusivity of gold in lead being 3·0 sq. centims. per day, at 500°. As already stated, Dr Guthrie<sup>1</sup> published, in 1883, particulars of some experiments of this kind, the metals he selected being zinc, tin, lead, sodium, and potassium, diffusing in mercury. He did not make any calculations with a view to obtain either the absolute or the relative diffusivities of these metals in mercury; indeed, after giving the percentage of the diffusing metal in successive quantities of mercury, he observes: "It is scarcely worth while dividing these diffusion *percentages* by the so-called atomic weights of the metals." His experiments were complicated by the fact that in some cases he employed solid metals instead of fluid amalgams, as the source of the diffusing metal. Approximate results have, however, been obtained from his data, and from certain measurements of the original apparatus, now deposited in the South Kensington Museum. These show that his inference "that potassium and sodium have a far greater diffusive energy than the heavier metals examined" is not supported by the actual result of his experiments. His results, calculated by the method given in the present chapter, give the values of *k* in sq. centims. per day as follows:—

Tin in mercury at about 15° . . . . .	1·22
Lead . . . . .	1·0
Zinc . . . . .	1·0
Sodium . . . . .	0·45
Potassium . . . . .	0·40

The diffusion of certain metals in mercury has also been studied by Humphreys,<sup>2</sup> whose results substantially confirm those of Guthrie, and more recently by Wogan,<sup>3</sup> who gives

<sup>1</sup> *Phil. Mag.*, vol. xvi., 1883, p. 321.

<sup>2</sup> *Trans. Chem. Soc.*, 1896, p. 243 and p. 1679.

<sup>3</sup> *Ann. de Physik*, 23, ii. p. 345, 1897.

the following figures for the value of  $k$  at the temperatures stated :—

	Temperature.	$k$ .		Temperature.	$k$ .
Lithium . .	8·2	·66	Zinc . .	11·5	2·19
Sodium . .	9·6	·64	„ . .	99·2	2·90
Potassium . .	10·5	·53	Cadmium . .	8·7	1·45
Rubidium . .	7·3	·46	„ . .	99·1	2·96
Cæsium . .	7·3	·45	Lead . .	9·4	1·50
Calcium . .	10·2	·54	„ . .	99·2	1·92
Strontium . .	9·4	·47	Tin . .	10·7	1·53
Barium . .	7·8	·52	Thallium . .	11·5	·87

With regard to the diffusivity at high temperatures, he found that all metallic amalgams, with the exception of zinc, cadmium, and lead, attacked the glass vessels.

**Volatility of Metals.**—The diffusion of metals in each other must be closely connected with the evaporation of solid metals or alloys at temperatures far below their melting-points. It is not necessary to go further back for definite views on the subject than to the time of Boyle,<sup>1</sup> who thought that “even such (bodies) as are solid may respectively have their little atmospheres, . . . for,” he adds, “no man, I think, has yet tried whether glass, and even gold, may not in length of time lose their weight.”

Boyle's opinion was correct, for mercury which has been frozen by extreme cold does, as Merget<sup>2</sup> showed two centuries later, evaporate into the atmosphere surrounding it; a fact which is of much interest in connection with Gay-Lussac's well-known observation that the vapours emitted by ice and by water both at 0° C. are of equal tension. Demarcay<sup>3</sup> has proved that *in vacuo* metals evaporate sensibly at lower temperatures than they do at the ordinary atmospheric pressure, and he suggested that even metals of the platinum group will be found to be volatile at comparatively low temperatures, a fact which has been well established by recent work. Holborn and Henning<sup>4</sup> have shown that platinum, iridium, and rhodium lose weight appreciably at high temperatures. Thus, when maintained at a white heat for eight hours, weighed pieces of iridium lost 70 milligrams, platinum 7, rhodium 6, platinum-iridium alloy containing 10 per cent. of iridium 24, and a similar platinum-rhodium alloy lost 9 milligrams. With regard to the volatilisation of metals *in vacuo*, Krafft<sup>5</sup> has published interesting figures which confirm the work

<sup>1</sup> Collected works, Shaw's edition, 1738, i. p. 400.

<sup>2</sup> *Ann. de Chim. et de Phys.*, vol. xxv., 1872, p. 121.

<sup>3</sup> *Comptes Rendus*, vol. xcv., 1882, p. 183.

<sup>4</sup> *Preuss. Akad. Wiss. Berlin Sitz. Ber.*, xxxix. p. 936, 1902.

<sup>5</sup> *Ber. Deut. Chem. Gesell.*, xxxviii. p. 262, 1905.



of Demarcay and Spring,<sup>1</sup> the following table being taken from his work :—

	Temperature at which Evaporation begins <i>in vacuo</i> .	Boiling-point <i>in vacuo</i> .	Boiling-point at 760 mm.
Mercury . . .	- 40	155	357
Cadmium . . .	156	450	749
Zinc . . .	184	550	920
Potassium . . .	63	365	667
Sodium . . .	98	418	742
Bismuth . . .	270	993	1700
Silver . . .	680	1360	2040

Some very interesting work has recently been done on the volatilisation of solids at the ordinary temperature, and Zenghelio<sup>2</sup> claims to have proved that lead, copper, and many metallic compounds volatilise appreciably in the course of time. In these experiments, silver leaf was hung over the solid body under observation, in a desiccator, for lengths of time up to six months, and he found that he could then determine the volatilised metal in the silver.

**Magnetic Properties of Metals.**—The fact that metals differ widely in their behaviour when placed in a magnetic field is well known. When considering magnetic properties, it has been customary to speak of metals as being either paramagnetic or diamagnetic. Paramagnetic bodies are such that, if a bar be presented to a north-seeking pole of a magnet, a south-seeking pole is induced on the nearer end, attraction results, and the magnetised bar tends to move into the stronger part of the field. On the other hand, diamagnetic bodies are such that, if presented to a north-seeking pole of an intense magnetic force, a north-seeking pole is induced on the nearer end, repulsion follows, and the bar tends to move into the weaker parts of the field. Again, paramagnetic bodies are such that if a strip be freely suspended from its centre and placed in a magnetic field, the induced magnetism causes it to set itself parallel to the direction of the magnetising force. On the other hand, diamagnetic bodies under similar conditions tend to take up a position at right angles to the direction of the magnetic force.

Thus, iron, nickel, and cobalt are typically paramagnetic, while copper and bismuth are diamagnetic. This is otherwise stated by saying that the magnetic permeability of iron, nickel, and cobalt is greater than that of air, while that of copper and bismuth is less.

<sup>1</sup> *Comptes Rendus*, 1894, p. 42.

<sup>2</sup> *Zeitschr. Phys. Chem.*, i. p. 219.



The magnetic permeability of any substance is the ratio of the induction to the magnetising force, and is generally indicated by

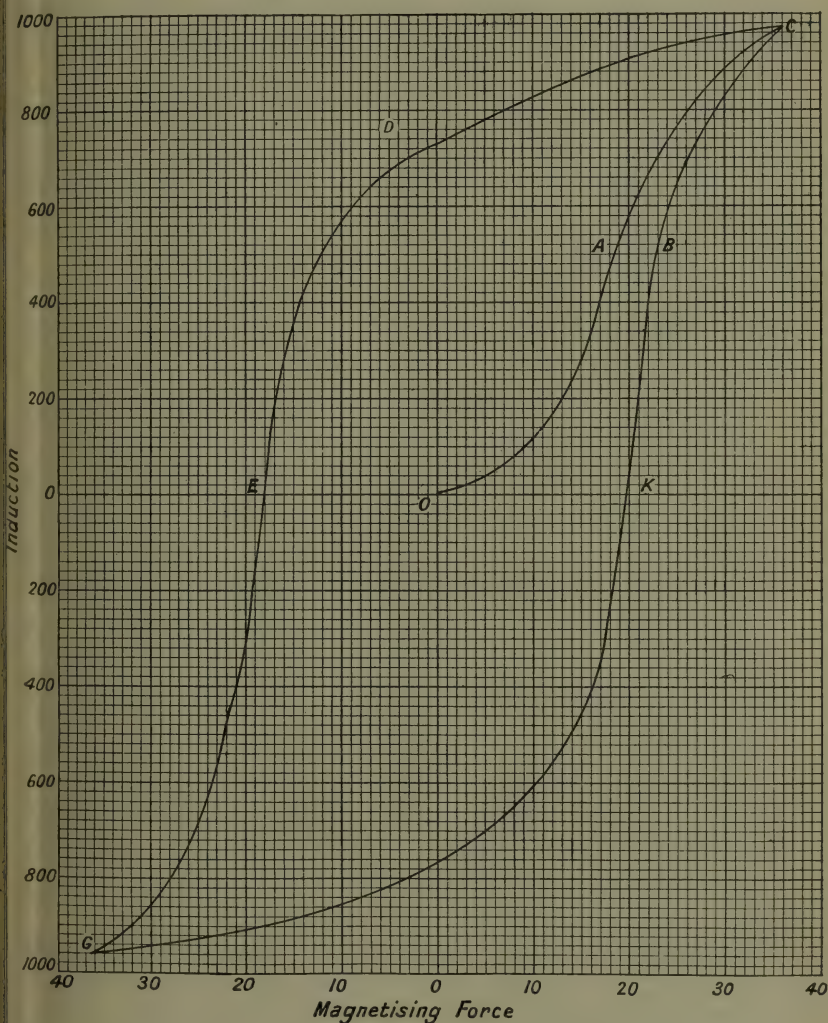


FIG. 21.

the letter  $\mu$ . The induction is measured by applying various magnetising forces to the specimen under examination, either in the form of wires or as closed rings, the intensity of the magnetisation being measured by a magnetometer when wires

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<sup>2</sup> *Zeitschr. Phys. Chem.*, 1. p. 219.

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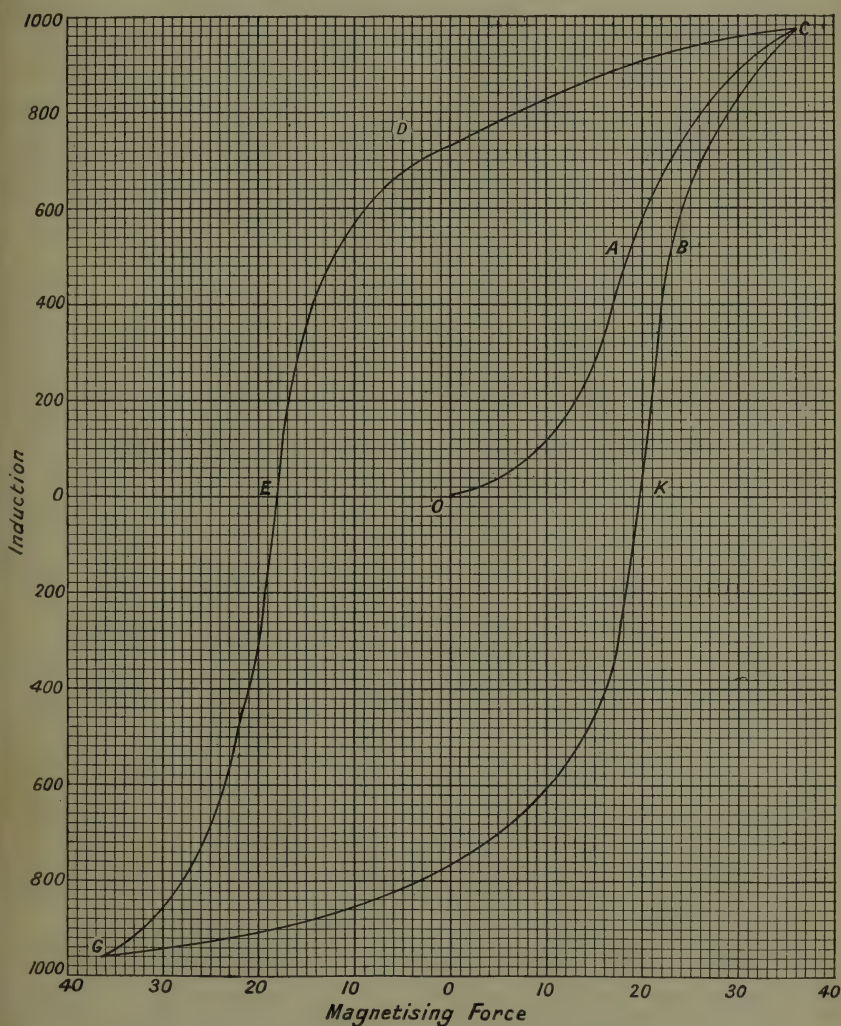


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are used, or by means of a ballistic galvanometer in the case of closed rings. Retentivity is the property magnetic bodies possess of retaining a large proportion of the total magnetisation after the magnetising force has been removed.

Hysteresis is the term applied to the well-known phenomenon of the magnetisation of a body lagging behind the magnetising force. This may be well illustrated by the examination of fig. 21, which is a hysteresis curve of a steel wire.

If, starting with an unmagnetised bar of iron or steel, we gradually increase the magnetising force and determine the corresponding values of the induction, we shall obtain a curve similar to OAC in the figure. When the point C is reached, assuming the magnetising force is gradually decreased and the value of the induction is again measured as the magnetising force decreases, it will be found that the curve obtained does not coincide with the curve obtained as the magnetising force increases, but has the form CD; thus, when the magnetising force is zero, the induction, instead of being zero, has the value OD.

On reversing the direction of the magnetising force, the curve DEG will be obtained; and on decreasing the magnetising force to zero, and then starting with it in its original direction, the branch GKBC of the curve will be obtained. The magnetising force represented by OE or OK denotes the force required to deprive the bar of its residual magnetisation.

When a bar of iron or steel is heated to redness, it loses its power of becoming magnetised, or if permanently magnetised, all this permanent magnetism will be lost. Similar changes take place in the case of nickel and cobalt. The temperature at which metals lose their magnetic properties is called the critical temperature, and in the case of iron and carbon steels corresponds with  $A_{r_2}$  point, being about  $770^{\circ}$  C. (see Chapter IV.).

For nickel the critical point is at about  $300^{\circ}$ , and when nickel is alloyed with iron some very peculiar magnetic effects may be produced; thus a special steel containing 25 per cent. of nickel is unmagnetisable at ordinary temperatures; if, however, it be cooled down to a temperature a few degrees below zero it becomes magnetisable, and this magnetisation is retained up to a temperature of  $580^{\circ}$ , when it again becomes non-magnetic, and remains in this state until it has again been cooled below zero.

The question of soft iron for the armature cores of dynamos is one of great importance to the electrical engineer, the aim being to attain high permeability but low retentivity.

Not only has the chemical composition to be considered, but also the thermal and mechanical treatment. The exact conditions of annealing<sup>1</sup> which will give the best effect, that is, the minimum

<sup>1</sup> Hans Kemp, *Stahl und Eisen*, Dec. 1 and 15, 1899, trans. by Dr R. Moltenke. *Iron Trade Review*, Feb. 15, 1900.—Madame Curie, "Magnetic Properties of Hardened Steels," *Bull. Soc. d'Encouragement pour l'Ind. Nat.*



hysteresis loss, seem to depend on the rate of cooling, but to be independent of the rate of heating.

**Electrical Resistance of Metals.**—The resistance of a conductor is the ratio of the electromotive force applied at its ends to the current passing, and it follows from this that a conductor has unit resistance when unit difference of potential produces unit current in it. The unit of resistance is the ohm, and is such that the E.M.F. between the terminals of a conductor of which the resistance is one ohm, when a current of one ampere is passing through it, is one volt. The ohm is equal to  $10^9$  c.g.s. units.

In metallic conductors, the resistance varies with the nature of the material, the dimensions of the conductor, and the temperature. For a wire of a given material, under constant temperature, the resistance is found to be directly proportional to the length, and inversely proportional to the cross section. The specific resistance of a metal is the resistance of a length of one centimetre with a cross section of one square centimetre. The reciprocal of the resistance of a conductor is known as its conductivity.

In the following table the specific resistance of some pure metals is given, but it must be remembered that a minute trace of impurity may very largely influence this property. The specific resistance also depends to a considerable extent on the state of the material as to hardness produced by work on it, or the conditions of annealing if this hardness has been removed by annealing.

#### SPECIFIC RESISTANCE OF METALS.

Metal.	Resistance in Ohms of a Rod 1 cm. long and 1 sq. cm. Cross-section at 0° C. $\times 10^6$ .
Silver . . . . .	1.50
Copper . . . . .	1.57
Gold . . . . .	2.24
Aluminium . . . . .	2.62
Magnesium . . . . .	4.31
Iron . . . . .	10.68
Platinum . . . . .	11.19
Nickel . . . . .	12.00
Lead . . . . .	19.80

*Commission des Alliages*, Jan. 1898; also in *Metallographist*, 1898, p. 107, and *Electrical Review*, Jan. 1899.—Osmond, "Steel for Magnets," *Comptes Rendus*, June 19, 1899; also *Metallographist*, 1900, p. 35.—Harbord and Twynam, "Hardening of Steel," *Journ. West of Scotland Iron and Steel Inst.*, 1898.—Osmond, "Magnetic Changes at  $Ar_2$  and  $Ar_0$ ," *Metallographist*, 1898, p. 158.—Barrett, Brown, and Hadfield, "On the Electrical Conductivity and Magnetic Properties of Alloys," *Trans. Roy. Dublin Soc.*, vol. vii., series ii., p. 67, 1900; *Proc. Inst. Elec. Eng.*, vol. xxxi. p. 674, 1900; *Trans. Roy. Dublin Soc.*, vol. viii., series ii., p. 1, 1902.

In the case of pure metals, the specific resistance always increases with increase of temperature. In the same manner the resistance decreases as the temperature is lowered, in such a way as to suggest that at absolute zero the resistance would be zero.<sup>1</sup> This, however, has proved to be incorrect, as Onnes and

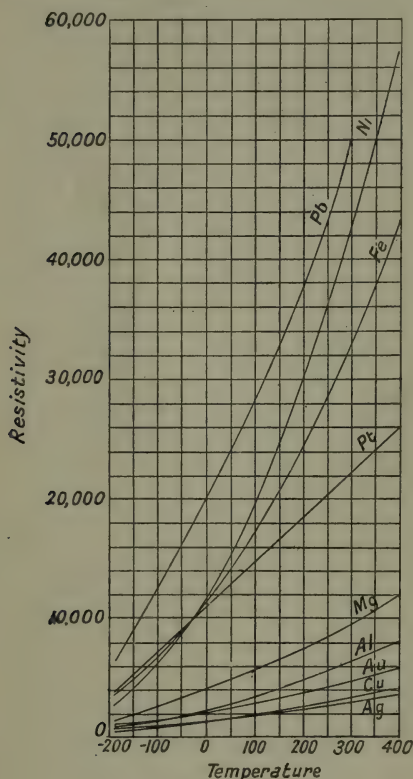


FIG. 22.

Clay have shown that at very low temperatures points of inflection occur, and it is probable that points of minimum value are reached at low temperatures, after which an increase in resistance is obtained.

Niccolai<sup>2</sup> has recently determined the resistance of metals between the temperatures 400° and -189°, and from his results the curves in fig. 22 are deduced.

**Specific Heat of Metals.**—The quantity of heat necessary to raise the temperature of 1 gramme of a substance through 1° C. at any given temperature is called the specific heat of the substance at that temperature.

Recent experiments by Tilden, Behn, and others show that the influence of temperature on the specific heats of metals is much greater than was formerly supposed.

The specific heat of metals increases in value as the temperature

<sup>1</sup> Dewar and Fleming, *Phil. Mag.*, vol. xxxiv., 1892, p. 326; vol. xxxvi. (1893), p. 271.

<sup>2</sup> *Accad. Lincei Atti*, xvi. p. 757, and also p. 906.

is raised and decreases in value as the temperature is lowered below  $0^{\circ}\text{C}$ . Harker<sup>1</sup> has determined the mean specific heat of iron between  $0^{\circ}$  and various high temperatures: between  $0^{\circ}$  and  $200^{\circ}$  he found it to be  $\cdot 1175$ , between  $0^{\circ}$  and  $850^{\circ}$  it had increased to  $\cdot 1647$ , but in the case of iron this increase is not continued at higher temperatures, for between  $0^{\circ}$  and  $1100^{\circ}$  a mean value of  $\cdot 1534$  only was obtained.

## PHYSICAL CONSTANTS OF METALS.

Metal.	Symbol.	Atomic Weight. 0=16	Atomic Volume.	Specific Gravity.	Specific Heat.	Melting-point. °C.	Coefficient of Linear Expansion.	Therm. Cond. C.G.S. Units.	Elect. Cond. C.G.S. Units.
ALUMINIUM .	Al	27.1	10.6	2.56	0.218	657	0.0000231	.502	390,000
ANTIMONY .	Sb	120.2	17.9	6.71	0.051	632	0.0000105	.042	31,471
ARSENIC . .	As	74.96	13.2	5.67	0.081	450 under pressure	0.0000055	..	32,425
Barium . . .	Ba	137.37	36.3	3.78	0.047	850			
BISMUTH . .	Bi	208.0	21.2	9.80	0.031	266	0.0000162	.019	9,091
CADMIUM . .	Cd	112.4	13.2	8.60	0.056	322	0.0000306	.219	99,800
CÆSIUM . . .	Cs	132.81	71.0	1.87	0.048	26	0.0001316	..	25,400
Calcium . . .	Ca	40.09	25.5	1.57	0.170	780	..	..	150,818
Cerium . . .	Ce	140.25	21.0	6.68	0.045	623			
CHROMIUM .	Cr	52.0	7.6	6.80	0.120	1482			
COBALT . . .	Co	58.97	6.9	8.50	0.103	1464	0.0000123	..	106,140
Columbium .	Cb	93.5	13.0	7.2	0.071	1950			
COPPER . . .	Cu	63.57	7.1	8.93	0.098	1084	0.0000167	.924	640,615
Gallium . . .	Ga	69.9	11.8	5.90	0.079	30			
Glucinum . .	Gl	9.1	4.7	1.93	0.621	Below 960			
GOLD . . . .	Au	197.2	10.2	19.32	0.031	1064	0.0000144	.700	455,166
Indium . . .	In	114.8	15.5	7.42	0.057	155	0.0000417	..	112,400
IRIDIUM . .	Ir	193.1	8.6	22.42	0.033	1950	0.0000070		
IRON . . . .	Fe	55.85	7.2	7.86	0.110	1505	0.0000121	.147	110,314
Lanthanum .	La	139.0	22.7	6.10	0.045	810			
LEAD . . . .	Pb	207.1	18.2	11.37	0.031	327	0.0000292	.084	49,067
Lithium . . .	Li	7.0	13.0	0.54	0.941	186	..	..	119,428
MAGNESIUM .	Mg	24.32	13.9	1.74	0.250	633	0.0000269	.343	229,616
MANGANESE .	Mn	54.93	7.3	7.50	0.120	1207			
MERCURY . .	Hg	200.0	14.7	13.59	0.032	- 39	0.0000610	.015	10,630
MOLYBDENUM	Mo	96.0	11.2	8.60	0.072	2500			
NICKEL . . .	Ni	58.68	6.7	8.80	0.108	1427	0.0000127	.141	144,196
Osmium . . .	Os	190.9	8.5	22.48	0.031	2500	0.0000065	..	105,300
Palladium . .	Pd	106.7	9.3	11.50	0.059	1535	0.0000117	.168	97,867
PLATINUM . .	Pt	195.0	9.1	21.50	0.032	1745	0.0000089	.166	91,600
POTASSIUM .	K	39.1	45.5	0.86	0.170	62	0.0000841	..	141,990
RHODIUM . .	Rh	102.9	8.5	12.10	0.058	1660	0.0000085		
Rubidium . .	Rb	85.45	55.8	1.53	0.077	38			
Ruthenium .	Ru	101.7	8.3	12.26	0.061	1800	0.0000096		
Scandium . .	Sc	44.1	17.6	2.5	0.153	1200			
SILVER . . .	Ag	107.83	10.2	10.53	0.056	962	0.0000192	.993	681,198
SODIUM . . .	Na	23.0	23.8	0.97	0.290	95	0.0000710	.365	253,973
Strontium . .	Sr	87.62	34.5	2.54	..	800	..	..	45,708
Tantalum . .	Ta	181.0	14.1	12.8	0.033	2910	0.0000079	..	60,600
Tellurium . .	Te	127.5	20.4	6.25	0.049	440	0.0000167	..	46,600
Thallium . .	Tl	204.0	17.2	11.85	0.033	303	0.0000302	..	56,712
Thorium . . .	Th	232.42	20.9	11.10	0.028	1450			
TIN . . . . .	Sn	119.0	16.3	7.29	0.055	232	0.0000232	.155	76,640
Titanium . .	Ti	48.1	13.5	3.54	0.13	2000?			
TUNGSTEN . .	W	184.0	9.6	19.10	0.034	3100			11,600
URANIUM . .	U	238.5	12.8	18.7	0.028				
VANADIUM . .	V	51.2	9.3	5.50	0.125	1680			
Yttrium . . .	Yt	89.0	23.4	3.80		1000?			
ZINC . . . .	Zn	65.37	9.1	7.15	0.094	419	0.0000291	.269	171,381
Zirconium . .	Zr	90.6	21.8	4.15	0.066	1500			

<sup>1</sup> *Phys. Soc. Proc.*, xix. p. 703, 1905.

## NOTES ON THE TABLE OF PHYSICAL CONSTANTS OF METALS.

The atomic weights given are those approved by the International Congress for the year 1910 (see *Proc. Chem. Soc.*, vol. xxv., No. 362, p. 255). The atomic volumes have been calculated from the latest figures for atomic weights and specific gravities. The specific heats given are the mean specific heats between 100° and 15° in most cases. Great care has been taken to obtain the latest and most trustworthy figures for the melting-points. The thermal conductivities are given in calories, centimetre-seconds; when multiplied by 100, the figures obtained are practically the same as when silver is taken as the standard with a conductivity of 100. The electrical conductivities are given in absolute units measured in mhos. Mhos are the reciprocals of ohms, and the mho-conductivity is obtained by dividing  $10^9$  by the volume resistivity in c.g.s. units.



## CHAPTER III.

### ALLOYS.

**Early Investigations.**—Many valuable mechanical properties are conferred upon metals by associating them with each other—this fact was discovered at a very early period of metallurgical history, and it seldom happens that metals are used in a state of purity when they are intended for industrial purposes. The word “alloy” originally comes, in all probability, from the Latin *adligo* (alligo), “to bind to,” and not, as Sir John Pettus thought, from the Teutonic *linderen*, “to lessen,” suggestive as it is of the fact that a precious metal is lessened in value by the addition of a base one.

The distinguished chemist Dumas eloquently pleaded, many years ago, against leaving alloys in the oblivion to which modern chemists consigned them. Until quite recently the extent and complexity of the subject was not realised, and Lupton,<sup>1</sup> in 1888, directed attention to the number of alloys which then awaited examination. He said:—“Hatchett recommended that a systematic examination of all possible alloys of all the metals should be undertaken. He forgot to remind anyone who should attempt to follow his advice that if only one proportion of each of the thirty common metals were considered, the number of binary alloys would be 435, of ternary 4060, and of the quaternary 27,405. If four multiples of each of the thirty metals be taken, the binary compounds are 5655, ternary 247,660, and quaternary 1,013,985.”

Nevertheless, if the properties of many alloys have yet to be investigated, the study of alloys generally has not been neglected. The modern bibliography relating to them is much more extensive than it is usually supposed to be, and the older writings are very full, and contain the results of far more accurate observation than they are credited with. In the early days of chemistry, as its history abundantly proves, alloys received much attention; and

<sup>1</sup> *Nature*, vol. xxxvii., Jan. 5, 1888, p. 238.

although the early chemists often failed to distinguish alloys from simple metals, or used them in unsuitable ways, they left an experimental record, the value of which is sadly unappreciated. From this record it is, incidentally, evident that the development of the art of separating metals from their ores, and from each other, was quickly followed by the acquisition of the knowledge that metals possess peculiar properties when reunited in certain proportions, and are thereby rendered more useful than they were in the pure state.

In early times some metals were used unalloyed, although at the present day they have little industrial application except in union with other metals. Antimony, for instance, now only employed as a constituent of certain alloys, was formerly cast and fashioned into ornaments, as is proved by the analyses of Virchow, and by a fragment of a very ancient Chaldean vase, which fragment, when examined by Berthelot, proved to be of pure antimony.<sup>1</sup> The implements and ornaments discovered by Schliemann abundantly show that the early Greeks were familiar with alloys of silver and gold, copper and tin, lead and silver, and with many others, all artificially prepared. Throughout the Middle Ages there seems to have been a belief that the action of metals on gold and silver was, on the whole, corrupting; and Biringuccio, in 1540, possibly seeing that this was the prevailing view, carefully defined such alloys as being "nothing but amicable associations of metals with each other"; and he further pointed out that metals must be mixed by weight, and not at random.

**Views as to the Constitution of Alloys.**—Passing from the sixteenth to the eighteenth century, we find four writers whose names deserve to be specially mentioned, because they seem to have been the first to indicate the direction in which modern investigation has been conducted. These are Réaumur, Gellert, Musschenbroek, and Achard, who respectively studied—1st (Réaumur), molecular change produced in a metal by heat; 2nd (Gellert), the relation of fluid metals to each other considered as solvents; 3rd (Musschenbroek), the cohesion of alloys as shown by certain mechanical properties; and 4th (Achard), the electrical behaviour of metals and alloys. It is interesting to trace the connection between the older work and the new. Réaumur,<sup>2</sup> in explaining the hardening of steel by rapid cooling from an elevated temperature, comes very near the modern view that a metal may, under certain conditions, pass from one allotropic state to another, for he distinctly contemplates the possibility of molecular change produced by the expulsion by heat of "sulphurs and salts" from the molecules into interstitial spaces between them. He speaks of "molecules and elementary parts

<sup>1</sup> *Ann. de Chim. et de Phys.*, vol. xii., 1887, p. 135.

<sup>2</sup> *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 321.

of molecules," like a modern writer, and tries to show that when hot steel is rapidly cooled, "sulphurs and salts" cannot return into the molecules, but remain in the interstitial spaces; and that, therefore, the physical properties of hard steel become quite different from those of soft. If it should be urged that the analogy between carburised iron and alloys is overstrained, it may be pointed out that, in 1867, Matthiessen said, after appealing to the fact that in certain alloys the constituent metals are present in allotropic states, "I have always made a comparison between iron and steel (and alloys). This has been done to show that the carbon iron alloys behave in an analogous manner to other alloys, which cannot be looked upon as chemical combinations."<sup>1</sup>

Gellert makes the analogy of certain alloys to solutions very clear, and in his *Metallurgic Chemistry* he gives a table showing the relative solubilities of metals in each other, while in the observations which accompany it<sup>2</sup> he says, to cite one of the cases he takes as an illustration, "Since copper and silver and copper and gold dissolve one another very readily, the copper cannot be parted from gold or silver by means of iron," probably having in mind a reaction which enables silver to be parted from gold by the action of sulphur and iron. He further clearly shows that, with regard to the solution of metals in a triple alloy, he understood the possibility of a division of a metal between two other metals acting as solvents.

The mechanical properties of alloys were investigated by Musschenbroek, who, working in the early part of the eighteenth century, made some experiments on the tensile strength of metals and alloys. He writes of "the absolute cohesion by which a body resists fracture when acted upon by force drawing according to its length," and gives the tenacity of several metals, and the alloys, brass and pewter.<sup>3</sup> He shows the importance of such work so clearly that it is remarkable how slowly the mechanical testing of metals has developed since his time.

Achard, whose researches were published in 1784, made a very extended series of experiments on multiple alloys, as well as those of simple metals. He pointed out that the relative conductivities of substances for heat and for electricity are closely related.<sup>4</sup> He devised an appliance for the experimental verification of this fact, and, as he included alloys in his researches, it may fairly be claimed that he led the way for the important generalisation that alloys may be ranged in the same order as regards their power of

<sup>1</sup> *Journ. Chem. Soc.*, 1867, p. 220.

<sup>2</sup> English translation of his work, London, 1776, p. 186.

<sup>3</sup> *Elements of Philosophy*, translated by John Colson, F.R.S., vol. i., 1744, p. 237.

<sup>4</sup> *Sammlung physikalischer und chemischer Abhandlungen*, Berlin, 1784, vol. i.



conducting heat and electricity which was made by Wiedemann and Franz in 1853-9.

The necessity of metals being pure when added to each other was hardly recognised until the eighteenth century ; and Duhamel, who contributed the article on alloys to the *Encyclopédie Méthodique* in 1792, appears to have been the first writer to insist on the necessity for making exact experiments upon alloys with metals which possess a high degree of purity, and on effecting their union by heat in closed vessels. He further pointed out that up to his time no chemist had taken these precautions, and it is certain that in conducting some modern experiments they have been neglected.

In the early part of the nineteenth century researches on alloys became more numerous ; they were mainly directed to ascertaining the effect on the density of metals produced by alloying them, and to determining the effects of slow cooling on alloys with low melting-points. Of such a nature was the work of Ermann in 1827 and of Rudberg (1830-1). Ermann called attention to the peculiar behaviour of alloys of lead and tin when solid. Rudberg studied anomalies in these alloys when in the liquid state.

Regnault showed that the specific heats of certain fusible alloys were greater near  $100^{\circ}$  than the mean specific heat of their constituents ; and this fact appears, as Spring has shown,<sup>1</sup> to have induced Person to undertake researches on the latent heat of alloys and on these specific heats.

Undoubtedly, one of the greatest works on alloys of the present century was that of Matthiessen, who studied the electrical resistance of metals and alloys, and was led to the conclusion that in many cases metals are present as allotropic modifications—that is, in totally different forms from those in which we ordinarily know them.

It is by no means easy to investigate the molecular constitution of alloys, but evidence may be gathered in the following ways :—

1. By comparing the properties of an alloy with those of its constituent metals.

2. By studying the behaviour of alloys in passing from the liquid to the solid state, and conversely in passing from the solid to the liquid.

3. By determining the physical constants of solid alloys, such as the melting-point, specific gravity, specific heat, electrical resistance, electromotive force, and their mechanical properties, such as tenacity and extensibility.

4. By examining with the microscope, suitably prepared surfaces of alloys, after various thermal and mechanical treatments.

First we must consider the methods of producing alloys, for the union of metals may be effected in three ways :—

<sup>1</sup> *Bull. de l'Académie Royale de Belgique*, 1886 (3), vol. xi. p. 355.



1. By fusion—that is, by causing metals to unite by melting them together.

2. By compression of the powders of the constituent metals.

3. By electro-deposition.

**Union of Metals by Fusion.**—The first method, by fusion, is naturally the method ordinarily adopted. One of the metals is melted, and the other is added to it, sometimes in the fluid state, but often in the solid. The product—the alloy—will have very different properties from those possessed by either of the constituent metals. Every metal has, of course, a definite melting-point, but, apart from the heat initially required to melt a metal, we find that the union of metals is sometimes attended with an evolution and sometimes with an absorption of heat.

The following metals evolve heat when they are united:—aluminium and copper, platinum and tin, arsenic and antimony, bismuth and lead, gold and just-melted tin; while, on the other hand, lead and tin absorb heat when their union takes place. There are many other cases.

In the case of many metals these effects can only be demonstrated by the aid of delicate instruments. There is, however, a simple case in which the union of metals is attended with a considerable diminution of temperature; it is an experiment we owe to Mohr, and its explanation is a very complicated one.

If tin, lead, and bismuth, as finely divided as possible, be intimately and rapidly mixed in equivalent proportions, with eight equivalents of mercury, under conditions in which heat is not transmitted to the mixture from the walls of the containing vessel, it will be found that the temperature falls from the ordinary temperature of the room + 17° C. to - 10° C., so that if a vessel containing water be placed in the mixture the water will be frozen. The experiment proves that by the union of metals, using mercury as a solvent, a freezing mixture may be produced.

**Union of Metals by Compression.**—For many years the labours of Prof. Walthère Spring, of the University of Liège, were largely devoted to the study of the effect of compression on various bodies.<sup>1</sup>

The particles of a metallic powder left to itself at the ordinary atmospheric pressure will not unite, but by augmenting the points of contact in a powder the result may be very different. Spring's experiments were made with the aid of a compression apparatus, the general form of the appliance employed being shown in the diagram, fig. 23. The metallic powder is placed under a short cylinder of steel, A, in a cavity in a steel block divided vertically, held together by a collar, and placed in a chamber of gun-metal,

<sup>1</sup> *Bull. de l'Académie Royale de Belgique* (2), vol. xlv. (1878), No. 6; (2), vol. xlix. (1880), No. 5. See also subsequent papers in the same publication, in the *Bull. Soc. Chim.*, Paris, and in the *Berichte der Deutsch. Chem. Gesellschaft* (Bildung von Legirungen durch Druck), vol. xv. p. 595.

which may be rendered vacuous. The pressure is applied to a cylindrical rod passing through the stuffing-box. Under a pressure of 2000 atmospheres on the piston, or 13 tons on the square inch, lead, in the form of filings, becomes compressed into a solid block, in which it is impossible to detect the slightest vestige of the original grains, while under a pressure of 5000 atmospheres lead no longer resists the pressure, but flows, as if it were liquid, through all the cracks of the apparatus, and the piston of the compressor descends to the base of the cylindrical hole, driving

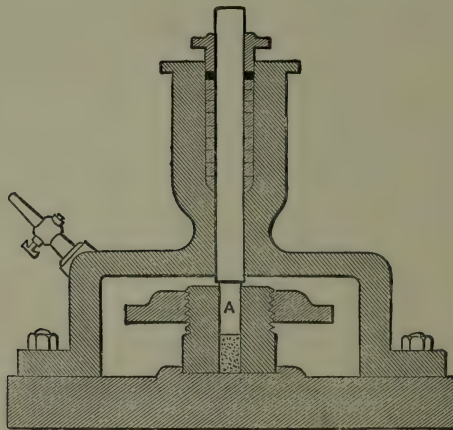


FIG. 23.

the lead before it. The more interesting results were obtained by Spring with crystalline metals. Bismuth, as is well known, is crystalline and brittle, yet fine powder of bismuth unites, under a pressure of 6000 atmospheres, into a block very similar to that obtained by fusion, having a crystalline fracture. Tin when compressed in powder unites; and if it is made to flow through a hole in the base of the compression apparatus, the wire so formed sometimes, though not always, emits the peculiar "cry" of tin when bent. The following table shows the amount of pressure required to unite the powders of the respective metals:—

					Tons per Square Inch.
Lead	.	.	.	unites at	13
Tin	.	.	.	"	19
Zinc	.	.	.	"	38
Antimony	.	.	.	"	38
Aluminium	.	.	.	"	38
Bismuth	.	.	.	"	38
Copper	.	.	.	"	33
Lead	.	.	.	flows at	33
Tin	.	.	.	"	47

We know that combinations are produced when certain bodies in solution are submitted to each other's action. But do solids combine? Is the alchemical aphorism "That bodies do not react unless they are in solution" true? Experiment proves that such solution is not necessary. Take, for example, two anhydrous salts—iodide of potassium and corrosive sublimate—both in a dry condition. When they are mixed in a mortar they unite, as is shown by the vermilion-coloured iodide of mercury which is produced. But do solid metals combine, in the sense in which chemical combination is possible between metals, when submitted to each other's action under the conditions which prevail when their powders are compressed? Mohr has pointed out<sup>1</sup> that cohesion is a form of chemical affinity; and the experiment cited of freezing water by the cold produced by amalgamation, affords valuable evidence in support of his view. It occurred to M. Spring that if there be true union between the particles of a metallic powder when submitted to great pressure in the appliance shown in fig. 23, it ought to be possible to build up alloys by compressing the powders of the constituent metals, and he urged that the formation of alloys by pressure would afford the most conclusive proof that there is a true union between the particles of metals in the cold when they are brought into intimate contact. Experiment proved that this reasoning is correct, for by compressing in a finely divided state fifteen parts of bismuth, eight parts of lead, four parts of tin, and three parts of cadmium, an alloy is produced which fuses at 100° C. It is necessary, however, to compress the mixed powder twice, crushing and filling up the block obtained by the first compression, because the mechanical mixture of the constituent metals is not sufficiently intimate to enable a uniform alloy to be obtained by a single compression. The alloy produced fuses in boiling water actually at 98° C., although the melting-point of the most fusible of its constituents, the tin, is 232° C. It may be urged that by compressing these powders heat is evolved, and that this heat may be sufficient to produce incipient fusion of the metallic powders, or, at all events, may exert a material influence on the result obtained. This objection has been experimentally anticipated by Prof. Spring. First the compression is effected with extreme slowness, and therefore there can be no question as to the sudden evolution of heat, as would be the case if the powders were compressed by impact instead of by slow squeeze; and, to sum the matter up briefly, Spring calculates an extreme case—that if it be granted that all the work done in compressing the powders were actually translated into heat, it would only serve to heat a cylinder of iron 10 mm. in height and 8 mm. in diameter (the dimensions of cylinder A, fig. 23, used in his apparatus) 40·64° C.

In order that direct experimental evidence might not be want-

<sup>1</sup> *Liebig's Ann.*, vol. xcvi. (1879), p. 183.



ing, Spring took the organic body, phorone, a hard, crystalline substance which melts at  $28^{\circ}$  C., and compressed it exactly as in the case of the metallic powders.<sup>1</sup> He took the precaution to place a shot of lead on the top of the powder before submitting it to compression. Only imperfect union of the particles of phorone resulted. The conclusion of the experiment proved that the shot remained where it had been placed at the top of the column, and therefore the  $28^{\circ}$  necessary to melt the substance had not been evolved, for if it had, the shot must have fallen through the fluid mass. It is, then, absolutely safe to conclude that, in the compression of bismuth for instance, there can be no question of the evolution of the heat necessary for the fusion of the metal.

It appears to be also quite safe to conclude that it is proven that *solid* metals possess the power of reacting on each other and forming alloys, provided their particles are really in contact.

**Union of Metals by Electro-Deposition.**—The formation of alloys by the electrolytic deposition of the constituent metals is a subject of great importance; and although the union of metals is usually effected by fusion, fire is not the only agent which can be employed for this purpose. Two or more metals can be deposited side by side by the aid of the electric battery. Copper and zinc may be deposited by electrolysis so as to form brass, and many of the beautiful bronzes and alloys of the Japanese can be obtained electrolytically; and, further, by suitable admixture of gold, silver, and copper, red gold, rose-coloured gold, or green gold may be deposited, so that the electro-metallurgist has at his command the varied palette of the decorative artist.

**Liquation and Segregation.**—It is now necessary to examine more closely the mutual relations of the metals when united. Metals may be mixed in the fused state, but it by no means follows that they will remain in admixture if they are allowed to cool slowly, or sometimes even rapidly. In fact, a cooling mass of mixed metals often behaves much as water containing suspended matter does in freezing, when the ice first formed rejects the foreign matter, and, as has been shown by the classical researches of Levol,<sup>2</sup> the portion of the alloy which first solidifies rejects certain other portions of the constituent metals. This action is called **liquation**. The term is also applied in a somewhat wider sense to the actual isolation of the components of ores or of alloys from each other. For instance, when an ore or mixture of metals is exposed to a degree of heat sufficient only to melt the most fusible member or constituent present in the mass, it flows away from the unmelted residue. In the case of alloys the importance of liquation has been fully recognised. If lead and zinc be thoroughly mixed in

<sup>1</sup> *Bull. Soc. Chim.*, vol. xli. (1884), p. 488.

<sup>2</sup> *Ann. de Chim. et de Phys.*, vol. xxxvi. (1852), p. 193; vol. xxxix. (1853), p. 163.



the fused state, and slowly cooled in a deep mould, the separation will be almost complete, and it will also be seen that it is easy to break off one corner at the side where the zinc has separated itself, and to flatten out another one, which shows it to be nearly pure lead. Take, again, the case of what was a triple admixture of lead, antimony, and copper, thoroughly mixed when fluid, and cooled in a cylindrical mould. The copper and the antimony unite, but they reject much of the lead, and drive it to the centre of the mass, so that the solidified cylinder, when broken across, presents a ring of the purple copper-antimony alloy surrounding a malleable core. Silver and copper alloys behave in a similar manner, but in any mixture of fused silver and copper, one particular alloy of these metals is formed, which is driven outward or inward in the cooling mass according to whether silver or copper is in excess in the bath. In all these cases the separation is never complete; the lead retains some 1.6 per cent. of zinc, and the zinc about 1.2 per cent. of lead. The copper and antimony retain a small amount of lead, and the lead a small amount of copper and antimony, as is shown by some very careful experiments of Dr E. J. Ball, to which reference has already been made. The solid mass in all these cases is a mixture of solidified solutions of the metals in each other.

Dr Guthrie investigated this side of the problem at some length.<sup>1</sup> It is difficult to give a brief account of his work, but his conclusions may be stated as follows: He considers that certain alloys in cooling behave as a cooling mass of granite would: clear molten granite would throw off, in cooling, "atomically definite" bodies, leaving behind a fluid mass, which is not definite in composition, as the quartz and the felspar undergo solidification before the mica. In alloys much the same thing happens, for when a molten mass of lead and bismuth or bismuth and tin cools, a certain alloy of the metals falls out, just as the quartz and felspar did, and ultimately the most fusible alloy of the series is left, which Dr Guthrie calls the eutectic alloy. It is the most fusible alloy of the series, but the proportions between the constituent metals are not atomic proportions, and Guthrie says that "the preconceived notion that the alloy of minimum temperature of fusion must have its constituents in simple atomic proportions, that it must be a chemical compound, seems to have misled previous investigators"; but he adds "that certain metals may and do unite with one another in the small multiples of their combining weight may be conceded; the constitution of eutectic alloys is not in the ratio of any simple multiple of their chemical equivalents, but their composition is not on that account less fixed, nor are their properties the less definite."

Guthrie dealt only with alloys of low melting-points, such as the fusible metals, but the facts are the same in the case of alloys

<sup>1</sup> *Phil. Mag.*, vol. xvii. (1884), p. 462.

with higher melting-points, as shown by later experiments. The silver-copper alloys, for instance, which melt below  $940^{\circ}\text{C}$ ., afford a striking instance. For further information upon this point we must wait for the development of Mendeléef's theory of solution. He regarded solutions as strictly definite, atomic, chemical combinations at temperatures higher than their dissociation temperatures. Definite chemical substances may be either formed or decomposed at temperatures above those at which dissociation commences; the same phenomenon occurs in solution; at ordinary temperatures they can either be formed or decomposed.

Liquation is very marked in the case of copper-silver alloys, and it is well known in Mints that when molten alloys of certain metals are cooled, groups of the constituent metals, or even the constituent metals themselves, separate, and thus occasion irregularity in the composition of the solidified mass. The phenomenon has been carefully studied by, amongst others, Lazarus Ercker

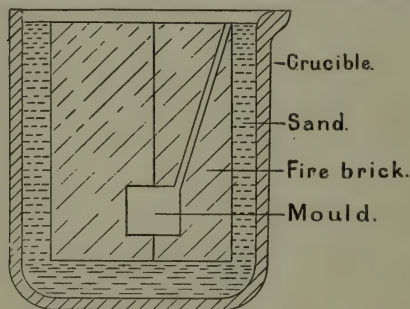


FIG. 24.

and Jars, whilst in more modern times the researches of D'Arcet in 1824, of Mercklein in 1834, of Levol in 1854, have shown that ingots of silver and copper are not homogeneous throughout. Levol cast the alloy to be examined either in a cubical iron mould of 45 mm. side, or in a sphere 50 mm. in diameter. He concluded that the only

homogeneous copper-silver alloy was that containing 71.89 per cent. of silver, and he considered this to be a definite combination of the two metals, with the formula  $\text{Ag}_3\text{Cu}_4$  (or  $\text{Ag}_3\text{Cu}_2$  if 63.57 be taken as the atomic weight of copper). All other alloys of silver and copper he viewed as mixtures of this definite alloy with excess of either of the metals. In 1875 the author<sup>1</sup> repeated many of Levol's experiments, and gave evidence for modifying his view that the only homogeneous alloy of silver and copper is that which contains 71.89 per cent. of silver. The uniformity in composition of the series of copper-silver alloys depends greatly on the method of cooling. By slow cooling, many alloys, other than the one mentioned above, may be made as uniform as it, its peculiarity consisting in the fact that its composition is uniform whether it is cooled slowly or rapidly. In order to ascertain whether liquation is modified if the cooling be greatly protracted, cubical moulds, about 4 to 5 millimetres in side, of firebrick (fig. 24), were employed. These could easily be heated to bright

<sup>1</sup> *Proc. Roy. Soc.*, vol. xxiii. (1875).

redness, and slowly and uniformly cooled. The following results show that the maximum difference in the composition of an alloy containing 925 parts of silver and 75 parts of copper was only 1·40 per thousand when the alloy was slowly cooled, while it was as much as 13 parts per thousand when the alloy was rapidly cooled:—

Vertical Plane	a.	925·7	Horizontal Plane	1.	924·8
	b.	925·0		2.	925·0
	c.	925·0		3.	924·9
	d.	925·0		4.	924·9
	e.	925·4		5.	925·0
	f.	924·3		6.	925·1
	g.	925·0		7.	925·1
	h.	925·3		8.	925·1
	i.	925·3		9.	925·0
	j.	925·3		10.	925·0
Vertical Plane	k.	924·3	Corners	α.	924·1
	l.	925·3		β.	924·1
	m.	925·3		γ.	924·1
	n.	924·4		δ.	924·4
	o.	925·0		ε.	924·0
	p.	924·3		ζ.	924·2
	q.	925·0		η.	924·2
	r.	925·3		θ.	924·9
	s.	925·0	"Dip Assay," 924·9.		
	t.	924·9			
Vertical Plane	u.	924·3	Maximum difference [between the centre and the corners], 1·40 per thousand.		
	v.	924·7			
	w.	924·9			
	x.	924·9			
	y.	925·3			

The diagram (fig. 25) shows the position in the cube corresponding to the letters and figures given above.

Levol also showed that in solidifying alloys of lead with the precious metals, if the latter are present in small quantity, they are driven towards the centre of the solidifying mass. Gowlan and Koga<sup>1</sup> have shown that when 984·37 parts of silver and 14·80 parts of bismuth are melted and cast into an open ingot mould so as to give an ingot weighing about 1000 troy oz., the portions of the ingot which remain longest fluid are richer in silver than the others. The entire question was reviewed in 1889 by Peligot,<sup>2</sup> who endeavoured to ascertain, by assaying various parts of an ingot of gold weighing 13 lbs., whether he could detect the

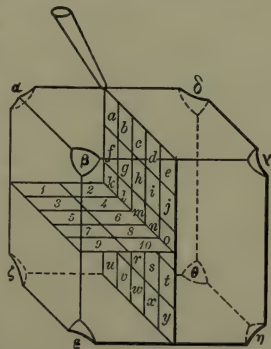


FIG. 25.

<sup>1</sup> *Journ. Chem. Soc.*, vol. li. (1887), p. 410.

<sup>2</sup> *Bull. Soc. d'Encouragement*, vol. iv. (1889), p. 171.



effects of liquation. The ingot contained 900 parts of gold in 1000, the alloying metal being principally copper, and he concluded that, within the limits of the errors of observation, there was no evidence of liquation. As this is a question of much industrial importance in relation to the precious metals, the author has made further investigations into the subject, and, in view of the difficulty of obtaining more precise evidence on the point, the following experiment was made: A gold ingot of a fineness of 984·7, the alloying metal being silver, was melted and poured into a spherical mould of iron. The temperature of the molten metal was much higher than that of the mould, and probably in this case the position of the metal which solidified last would be situated somewhere above the geometrical centre of the mass. From the sphere of solid gold, which was 3 in. in diameter and weighed 140 oz., a disc,  $\frac{3}{8}$  in. in thickness, and of the full diameter of the sphere, was cut in a vertical plane. This disc, which weighed 31 oz., was rolled in two directions, at right angles to each other, to a convenient thickness for cutting with shears, and assay pieces were cut from points distributed over its entire surface. The results of eighty-two assays afforded no clear evidence of systematic rearrangement, for although there appeared to be an enrichment towards the upper part to the extent of  $\frac{8}{100000}$ ths, such small differences as existed in the assays made on metal taken from the same horizontal planes could not be regarded as being due to any definite redistribution of the metal. It will thus be evident that gold of high standard alloyed with silver does not show any marked tendency to reject on solidification the silver with which it is associated. It is well known, however, that there is a development of crystallisation, and that other remarkable changes are produced in the structure of pure gold by the addition of minute quantities of lead, bismuth, and certain other metals. Ample evidence has been obtained by Dr T. K. Rose and the author<sup>1</sup> to show that gold alloyed with copper and properly mixed in the molten state is not homogeneous when solid. The importance of this fact is revealed by the opinion which has been expressed<sup>2</sup> that standard trial plates of gold alloyed with copper should no longer be used in testing the accuracy of the coinage.

Mr E. Matthey<sup>3</sup> has, moreover, shown that by casting an alloy of gold and platinum containing 900 parts of gold and 100 parts of platinum in the identical mould above described, there is a concentration of platinum towards the centre of the mass, the gold and platinum being as 900 gold to 98 platinum on the

<sup>1</sup> Rose, *Chem. Soc. Journ.*, vol. lxvii., 1895, p. 552. Roberts-Austen and Rose, *Proc. Roy. Soc.*, vol. lxvii., 1900, p. 105.

<sup>2</sup> *Annual Mint Report*, 1900.

<sup>3</sup> *Phil. Trans.*, [A] vol. clxxxiii. (1892), p. 629; *Proc. Roy. Soc.*, vol. xlvi. (1890), p. 180.



exterior, against 845 gold and 146 platinum at the centre of the mass. Consequently, it is evident that gold on solidifying does tend to free itself from associated platinum.

It is, however, in relation to the metallurgy of iron and steel that the question of liquation and segregation is of primary importance. There can be no doubt that when an ingot of steel slowly cools, phosphorus, sulphur, and carbon, and to a less degree manganese and silicon, tend to separate from the mass and to become concentrated in that portion of the ingot which solidifies last. The fact that segregation takes place in steel ingots appears to have been discovered by Stubbs,<sup>1</sup> who mentioned it, whilst discussing a paper by Parry, at the spring meeting of the Iron and Steel Institute, 1881. The subject was then taken up by Snelus,<sup>2</sup> who published his results in the same year, completely confirming Stubbs' earlier observations. Since then the subject has received attention from Eccles, Stead, Howe, Talbot, and others.

Talbot<sup>3</sup> made an exhaustive examination of segregation in acid and basic steel ingots, with and without the addition of aluminium. He concluded that in ingots to which no aluminium has been added, excessive segregation occurs down the central portion of the ingot, from about 6 inches from the top to half-way down, that sulphur tends to segregate most, phosphorus next, then carbon, and finally manganese, the segregation of which is so slight as to be almost negligible. The effect of the addition of 4 ounces of aluminium per ton was to immediately reduce the amount of segregation, as will be seen from the figures in the table on the next page, taken from analyses of borings from the centre and outside of acid steel ingots.

The borings were taken from top to bottom at distances of 6 inches, and the ingots measured 18 in. × 22 in. × 67 in.

The average analysis of all the drillings taken from the ingot to which no aluminium had been added was S·059 P·055 C·41; and the average analysis of all the drillings from the ingots to which aluminium had been added was S·060 P·052 C·39. There can be no doubt, therefore, that constituents whose presence is injurious to the mechanical properties of steel find their way towards the top centre of the ingot. In steel ingots destined for the manufacture of guns it is usual to cut off the tops, which are unsound as well as impure, and in some cases to bore out the centre of the ingot. For similar reasons, it is now customary to cut off the "crop" ends of steel rails. The importance of this procedure has been widely recognised,<sup>4</sup> and the effect of segrega-

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1881, i. p. 200.

<sup>2</sup> *Ibid.*, 1881, ii. p. 379.

<sup>3</sup> *Ibid.*, 1905, ii. p. 204.

<sup>4</sup> Maitland, *Min. Proc. Inst. C.E.*, vol. lxxxix. (1887), p. 127. See also Eccles, *Journ. Iron and Steel Inst.*, No. 1 (1888), p. 70, and the discussion on Greenwood's paper on the "Treatment of Steel by Hydraulic Pressure," *Min. Proc. Inst. C.E.*, vol. xeviii., 1889.

tion must be carefully considered in making large castings and forgings.

ANALYSES TAKEN FROM CENTRE AND OUTSIDE OF TWO INGOTS,  
FROM TOP TO BOTTOM, AT DISTANCES OF 6 INCHES APART.

No.	Without Aluminium.						With Aluminium.					
	Centre.			Outside.			Centre.			Outside.		
	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.	Carbon.	Sulphur.	Phosphorus.	Carbon.
Top.												
1	·053	·051	·41	·035	·047	·33	·038	·035	·32	·067	·054	·39
2	·049	·052	·39	·031	·034	·32	·042	·040	·35	·066	·057	·39
3	·267	·197	·95	·018	·030	·31	·078	·061	·48	·065	·056	·39
4	·141	·109	·59	·027	·036	·32	·086	·063	·43	·066	·055	·40
5	·097	·083	·47	·034	·040	·35	·081	·049	·34	·068	·067	·41
6	·081	·065	·46	·036	·046	·37	·059	·054	·38	·066	·058	·42
7	·056	·061	·46	·040	·048	·38	·067	·052	·38	·064	·057	·41
8	·056	·053	·38	·041	·046	·38	·057	·049	·36	·058	·052	·41
9	·043	·045	·35	·039	·044	·36	·053	·049	·36	·058	·056	·40
10	·048	·047	·35	·044	·046	·38	·056	·050	·36	·056	·056	·38
11	·047	·045	·34	·048	·048	·41	·057	·047	·37	·060	·053	·38
12	·051	·050	·39	·053	·054	·43	·056	·049	·38	·065	·054	·39
Bottom.												

Various methods have been introduced for compressing steel ingots while still in the fluid state, with a view of preventing segregation and lessening the amount of blowholes produced during the solidification. Casting under pressure was first attempted by Bessemer in 1856, but was reintroduced and rendered practicable by Whitworth in 1865;<sup>1</sup> more recently the Harmet<sup>2</sup> process of compressing steel ingots during solidification in vertical taper moulds, and the Robinson and Rodger<sup>3</sup> method of horizontal compression, have been introduced with considerable success, and both methods are successfully employed in various steelworks. All these methods very largely produce the desired results, giving greater homogeneity and freedom from blowholes, and greatly reducing the amount of cropping necessary.

In the case of pig-iron it is possible to isolate products of liquation, as has been shown by M. Lencauchez,<sup>4</sup> who heated fragments of iron to a temperature of 940° for 100 hours. At the end of this time a number of spherical grains sweated out from the surface of the fragments. Analysis of these exudations showed that they contained from 4 to 6 per cent. of phosphorus, from 0·6 to

<sup>1</sup> Patent No. 3018, 1865.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1902, ii. p. 146.

<sup>3</sup> Capron; *Journ. Iron and Steel Inst.*, 1906, i. p. 28.

<sup>4</sup> *Mém. Soc. Ing. Civils*, 1887.

0·8 per cent. of silicon, from a trace to 1·5 per cent. of graphite carbon, and from 0 to 1·24 per cent. of combined carbon. The original pig-iron contained about 3·5 per cent. of total carbon, 2·6 of silicon, and 1·9 of phosphorus. The composition of these exudations, therefore, is that of pig-iron impoverished in carbon and silicon, but considerably enriched in phosphorus. The question of the modes of existence of phosphorus in iron has been exhaustively studied and described by Stead.<sup>1</sup>

If lead, tin, and zinc are melted together, and left at rest in a fused condition, no separation takes place if the proportion of tin exceeds a certain amount; but if the quantity of tin is less than this, the alloy separates into two layers, each layer consisting of a ternary alloy of the three metals. Dr C. R. A. Wright and Mr C. Thompson<sup>2</sup> have examined the nature of this separation, and the composition of the alloys under different conditions. The heavier alloy, they found, consists of a saturated solution of zinc in lead containing tin, whilst the lighter consists of lead in zinc containing tin. The two alloys always correspond with two conjugate points on the solubility curves of zinc in lead-tin, and of lead in zinc-tin. The tin is not distributed equally in the two alloys, except when present in a particular proportion, which varies with the ratio of zinc to lead. With less tin than this, the lighter alloy takes up the excess of tin; with more, the heavier takes up the excess.

**Solution of Metals in Metals in the Fluid Condition.**—Many researches of late years have been made on this important and interesting subject, and the late Dr Alder Wright, F.R.S., originally prepared for this book the following account of his work in this direction.<sup>3</sup>

He stated that in the course of a series of experiments lasting over several years the following results were arrived at.

Of the 36 pairs which it is possible to form with the 9 metals Pb, Bi, Al, Zn, Sn, Ag, Sb, Cd, Cu, the great majority have been found to possess the property of *completely blending with one another so as to form a homogeneous fluid* stable for many hours when they are heated to such a temperature that the whole mass remains liquid. On cooling, segregation occurs in many cases during solidification. Five pairs, however, are exceptional when the components lie within the under-mentioned limits; when well intermixed by stirring, and then allowed to stand molten for some hours at an equable temperature (preferably by pouring the fluid mass into clay test-tubes heated to the required temperatures in a bath of molten lead), two alloys separate from one another; the denser consists mainly of the heavier metal, A, containing in solution a small quantity of the lighter metal, B, the amount

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1900, ii. p. 60.

<sup>2</sup> *Proc. Roy. Soc.*, vol. xlv. (1889), p. 461.

<sup>3</sup> *Proc. Roy. Soc.*, 1889–1893.



dissolved increasing with the temperature; whilst the lighter alloy consists, conversely, mainly of B, with a little A. Using the nomenclature proposed by Sir G. G. Stokes, these pairs of metals form *real* alloys only when employed outside of the limits stated, while within these limits they form *ideal* alloys only.

It must be remembered that the word *ideal* is used in the sense of imaginary or *unreal*, as the alloys probably do not actually exist; they give rise to mixtures that are incapable of permanently remaining homogeneous, being analogous to intimate emulsions of oil and water, or ether and water, rather than to true mutual solutions of alcohol and water. The term "stable" and "unstable" alloys may also be conveniently used to distinguish the two classes respectively.

I. *Mean Values of Limits for Lead and Zinc (Average of numerous Determinations).*

At about 650° C.	.	Between	$\left\{ \begin{array}{l} \text{Pb} = 98.76 \\ \text{Zn} = 1.24 \end{array} \right\}$	and	$\left\{ \begin{array}{l} \text{Pb} = 1.14 \\ \text{Zn} = 98.86 \end{array} \right\}$
" 800° C.	.	"	$\left\{ \begin{array}{l} \text{Pb} = 98.70 \\ \text{Zn} = 1.30 \end{array} \right\}$	"	$\left\{ \begin{array}{l} \text{Pb} = 1.57 \\ \text{Zn} = 98.43 \end{array} \right\}$

II. *Bismuth and Zinc.*

At about 650° C.	.	Between	$\left\{ \begin{array}{l} \text{Bi} = 85.72 \\ \text{Zn} = 14.28 \end{array} \right\}$	and	$\left\{ \begin{array}{l} \text{Bi} = 2.32 \\ \text{Zn} = 97.68 \end{array} \right\}$
" 750° C.	.	"	$\left\{ \begin{array}{l} \text{Bi} = 84.82 \\ \text{Zn} = 15.18 \end{array} \right\}$	"	$\left\{ \begin{array}{l} \text{Bi} = 2.47 \\ \text{Zn} = 97.53 \end{array} \right\}$
" 800° C.	.	"	$\left\{ \begin{array}{l} \text{Bi} = 84.17 \\ \text{Zn} = 15.83 \end{array} \right\}$	"	$\left\{ \begin{array}{l} \text{Bi} = 2.52 \\ \text{Zn} = 97.48 \end{array} \right\}$

III. *Lead and Aluminium.*

At about 800° C.	.	Between	$\left\{ \begin{array}{l} \text{Pb} = 99.93 \\ \text{Al} = 0.07 \end{array} \right\}$	and	$\left\{ \begin{array}{l} \text{Pb} = 1.91 \\ \text{Al} = 98.09 \end{array} \right\}$
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IV. *Bismuth and Aluminium.*

At about 800° C.	.	Between	$\left\{ \begin{array}{l} \text{Bi} = 99.72 \\ \text{Al} = 0.28 \end{array} \right\}$	and	$\left\{ \begin{array}{l} \text{Bi} = 2.02 \\ \text{Al} = 97.98 \end{array} \right\}$
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V. *Cadmium and Aluminium.*

At about 750° C.	.	Between	$\left\{ \begin{array}{l} \text{Cd} = 99.78 \\ \text{Al} = 0.22 \end{array} \right\}$	and	$\left\{ \begin{array}{l} \text{Cd} = 3.39 \\ \text{Al} = 96.61 \end{array} \right\}$
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Out of the above-mentioned 9 metals, 84 different combinations can be formed, taking them 3 at a time. Of these, 55 combinations invariably form *real* alloys when heated so that the whole mass remains liquid, whilst 29 give rise to *ideal* ternary alloys when the proportions in which the materials are used lie within certain limits. These limits are delineated graphically by a method due to Sir G. G. Stokes (see p. 86). A triangle (preferably equilateral) is drawn, at the three corners of which weights are supposed to be placed in the ratio of the relative quantities



of the 3 metals respectively present in a given mixture of them ; then this mixture is denoted by a point within the triangle representing the centre of gravity of the 3 weights of the metals. An *ideal* alloy gives rise to two "conjugate points," representing the heavier and lighter alloys respectively into which the mass divides itself ; the line joining the points is referred to as a "tie-line" or "tie." With a sufficiently extended series of observations at a constant temperature,  $T^\circ$ , with the metals in suitably varying proportions, the various pairs of conjugate points deduced map out an area inside the triangle corresponding with the limits of composition within which *ideal* alloys result, and outside of which *real* alloys are formed at the temperature  $T^\circ$ . The loci of the two series of points represent curves, conveniently designated "critical curves," indicating the boundary of this limiting area.

The 29 possible kinds of ideal ternary alloys above mentioned are divisible into two classes characterised by entirely different kinds of critical curves, and differently shaped areas enclosed by them.

In the first class (23 in number), calling the 3 metals respectively A, B, and C, 3 pairs can be taken, respectively AB, AC, and BC. Of these, one pair, AB, is "immiscible"—*i.e.* is one of the 5 binary combinations furnishing ideal alloys when mixed within the limits above stated ; or, in other words, A will mix in all proportions with C, as also will B with C ; but A will not mix in all proportions with B. The third metal, C, which will mix in all proportions with either A or B, is conveniently designated the "solvent" metal. The 23 combinations of this kind are—

A.	B.	C = "Solvent."
Pb ... ..	Zn	} either Sn, Ag, Sb, Cu, or Cd = 10
Bi ... ..	Zn	
Pb ... ..	Al	} either Sn, Ag, Sb, or Cu = 8
Bi ... ..	Al	
Cd ... ..	Al	either Sn, Ag, Sb, Cu, or Zn + 5
23		

The critical curves deduced at certain definite temperatures for the majority of these combinations have been recorded in various papers communicated to the Royal Society. In all cases, when the triangular delineation is effected with the immiscible metals A and B at the base, and the solvent metal C at the apex of the triangle, the two series of points respectively representing the heavier and lighter conjugate alloys formed in a series of experiments with gradually increasing proportions of solvent metal form two branches or portions of a single curve, rising upwards from the base line to a maximum elevation, and then descending again to the base ; so that the area enclosed by the critical curve is roughly a segment of an ellipse. The point where the two branches meet and merge into one another (or point where the

system of tie-lines dwindles down to a point and vanishes) is conveniently designated the "limiting point." As a rule this is not the highest point of the curve, but lies on one side or the other, nearer to the base.

Thus, in the annexed diagrams, fig. 26, L represents the limiting point, lying to the *right* of the highest point of the curve in the case of lead-tin-zinc alloys, and to the *left* in that of lead-silver-aluminium alloys, fig. 27.

As regards the two immiscible metals, it is noteworthy that the relative proportion in which they are present at the limiting point is not at all constant, but varies within pretty wide limits according to the nature of the solvent metal.

For the same temperature, and all other things being the same, the substitution of *aluminium* for *zinc* as lighter immiscible metal appears always to *raise* the critical curve—i.e. the limits with zinc as lighter metal lie *inside* the corresponding limits with aluminium. Thus the dotted line, No. 2, fig. 27, representing

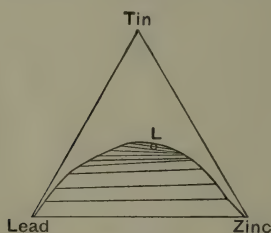


FIG. 26.

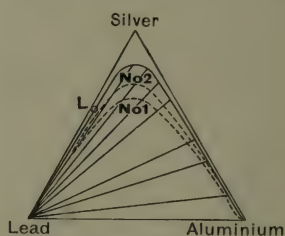


FIG. 27.

Pb, Ag, Al alloys, shows the corresponding curve obtained with Pb, Ag, Zn alloys, omitting bulges. A similar result is noticeable as regards *lead* and *bismuth*, the critical curve with bismuth as heavier immiscible metal always lying *inside* that similarly deduced with lead. On comparing curves obtained with the same immiscible pair at about the same temperature with the solvents *cadmium*, *silver*, *tin*, and *antimony* respectively, it is found that the cadmium and silver curves lie *outside* the tin curve, which again lies outside the antimony curve. Thus the dotted line, No. 1, in the figure representing Pb, Ag, Al alloys, indicates the corresponding curve obtained with Pb, Sn, Al alloys, lying well inside the continuous curve.

The second class of ternary alloys above referred to contains six members—

A.		B.		C.
Zn	...	Bi	...	Pb
Al	...	Bi	...	Pb
Bi	...	Al	...	Zn
Pb	...	Al	...	Zn
Al	...	Bi	...	Cd
Al	...	Pb	...	Cd

—the characteristic of this class being that *two* of the three pairs (AB and AC) are “immiscibles,” whilst the third pair (BC) consists of metals miscible in all proportions.

When the results of suitable series of observations are plotted with the metal A at the apex of the triangle (fig. 28), and B and C at the ends of the base, the two series of conjugate points trace out *two separate curves* that do not run into one another at a limiting point; one of these curves cuts off a 3-sided figure at the apex of the triangle bounded by the upper parts of the sides and this upper critical curve; the other similarly cuts off a 4-sided figure at the base, bounded by the base, the lower portions of the sides, and this lower critical curve; the area within which all points denote *ideal* alloys only is consequently a 4-sided figure bounded by the middle portions of the sides of the triangle, and the upper and lower critical curves, as indicated in the figure.

No less than 126 quaternary combinations can be formed out of the 9 metals above mentioned. Of these, 55 always form real alloys, whilst 71 give rise to ideal alloys when mixed in proportions inside certain limits. These limits may be delineated by supposing the 4 constituents to be placed at the 4 solid angles of a tetrahedron (preferably regular), when the centre of gravity of the whole is a point indicating the particular mixture used. The conjugate points furnished by a suitable series of ideal alloys map out a “critical surface” inside the tetrahedron.

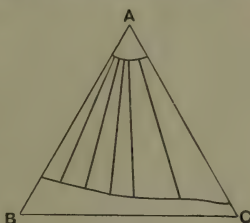


FIG. 28.

Since 6 pairs can be formed from the 4 constituents (AB, AC, AD, BC, BD, CD), 6 classes of quaternary ideal alloys can theoretically exist according as 1, 2, or more of these 6 pairs are “immiscibles.”

There are 126 quinary, 84 sexenary, 36 septenary, and 9 octenary combinations that can also be formed from the above 9 metals; making (with those above mentioned and the mixture of the whole 9) 502 different alloys in all. Of these, real alloys (no matter in what proportions the constituents are mixed) are afforded by only 31 quinary, 9 sexenary, and 1 septenary combinations, all the others furnishing ideal alloys when mixed in proportions not outside of certain limits. In all, 320 combinations out of the 502 possible ones can thus yield ideal alloys, whilst the other 182 combinations yield real alloys, no matter in what proportions they are mixed.

Dr Alder Wright's careful experiments also illustrate the similarity in the behaviour of molten alloys and ordinary solutions of salts. This subject has been reviewed by the author and Dr A. Stansfield.<sup>1</sup>

<sup>1</sup> *Sur la Constitution des Alliages Métalliques. Rapport présentés au Congrès International de Physique*, Paris, Gauthier Villars, vol. i., 1900, pp. 306-314.



**Action of Electric Currents on Molten Alloys.**—In tracing the analogies between alloys and saline solutions, it will be well to see what takes place when a current of electricity is passed through an alloy. Take first the case of a fluid alloy through which a current is passed. We have spoken of alloys as solutions; if they be ordinary chemical solutions it has been urged that an electric current of sufficient strength ought to decompose them, and it becomes a most important question to determine whether an ordinary metallic alloy can conduct electrolytically like a salt solution, or whether it conducts as a metal would, that is, without being decomposed.

The question therefore arises—Can a well-marked alloy, or a quasi-compound, be in the slightest degree electrolysed by an exceedingly intense electric current? Some experiments con-

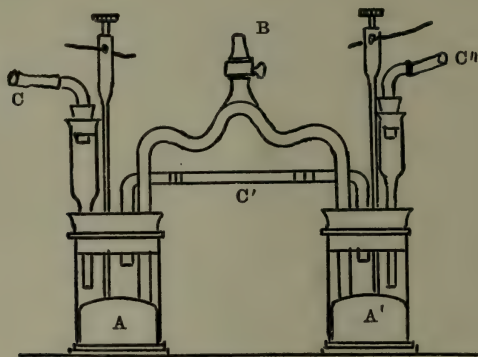


FIG. 29.

ducted by M. Gerardin<sup>1</sup> in 1861 satisfied him that amalgams of sodium and mercury might be decomposed by an electric current, with partial separation of the constituent metals. The experiments were repeated by Dr Obach,<sup>2</sup> who employed the apparatus shown in the diagram (fig. 29). The sodium amalgam is enclosed in the two glass vessels A A', and metallic communication between them is effected by opening the stopcock B and sucking the amalgam into the bent tube. An atmosphere of dry hydrogen is provided by the tubes C C' C'', and the current is transmitted through the amalgam by the battery terminals shown. Subsequent examination of the sodium amalgam proved that no separation had been effected. The composition of the amalgam was unaltered by the passage of the current. He also used a W-shaped tube containing melted alloys, and proved that

<sup>1</sup> *Comptes Rendus*, vol. liii. (1861), p. 727.

<sup>2</sup> *Poggendorff's Ann. der Phys. u. Chemie*, sup. vol. vii. (1876), p. 280.



no decomposition could be observed after the passage of the current.

In 1887, at the request of the Electrolysis Committee of the British Association, the author took up the inquiry,<sup>1</sup> and by employing an intense electric current from secondary cells, showed that no separation took place either in certain alloys of lead and gold, or in alloys of lead and silver, even with so strong a current as 300 amperes. The method employed is indicated by the diagram (fig. 30). The alloy, CD, under examination was placed in cavities cut in a firebrick, shown at E, and the cables from a secondary battery were connected by means of copper holders with wrought-iron terminals, AB. The experiments are given in detail in the *Report of the British Association for 1887*, and it will be sufficient to say here that, as the question at present stands, it would seem that fluid alloys conduct like metals, and not like salt solutions; but if, as Sir O. Lodge suggested, the question as to the possibility of the electrolytic separation of true alloys of metals should be answered in the negative, there must surely remain a group of bodies on the borderland between alloys proper and electrolytes, among which some gradual change from wholly metallic to wholly electrolytic conduction is to be looked for.

**Conduction of Electricity by Alloys at Varying Temperatures.**—It has long been known that the electrical resistance of alloys increases as the temperature is raised, and decreases as the temperature is lowered, but the want of a simple and accurate pyrometer for many years prevented experiments being carried far in this direction. Le Chatelier,<sup>2</sup> however, has shown by the aid of his pyrometer, to be hereafter described, that in metals which do not undergo any molecular change before fusion, the increase of electrical resistance is proportional to the temperature. Many metals seem, like iron, to undergo sharply defined molecular changes at definite temperatures, and some alloys show progressive changes, all of which are clearly indicated by abrupt or gradual change in resistances.

Dewar and Fleming<sup>3</sup> have examined the electrical resistances of a number of alloys at very low temperatures produced by means of liquid oxygen, and discovered the significant and important fact that although the resistance of alloys is decreased

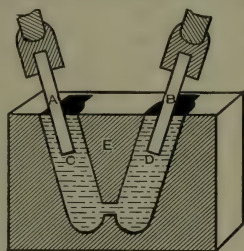


FIG. 30.

<sup>1</sup> *Report British Assoc.*, 1887, p. 341.

<sup>2</sup> *Comptes Rendus*, vol. cxi. (1890), p. 454.

<sup>3</sup> *Phil. Mag.*, vol. xxxiv. (1892), p. 326; vol. xxxvi. (1893), p. 271, in which some of the above results are slightly modified. See also *Engineer*, Jan. 27, 1893.

to a certain extent with a lowering of temperature, it is not decreased to the same extent as in the case of pure metals (see p. 66).

Niccolai<sup>1</sup> has recently determined the resistances of a number of alloys at temperatures varying from 400° C. down to -189° C, and from his figures the curves (fig. 31) have been plotted, showing the resistances in absolute magnetic units at different temperatures. Niccolai also showed that annealing and hardening not only altered the absolute value of the resistance, but

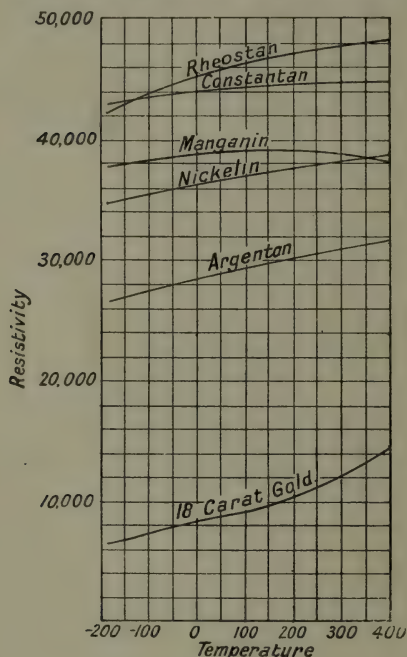


FIG. 31.

also altered the law of the variation of the resistance with temperature.

**Effect of Composition on the Conductivity of Metallic Alloys.**—The most important work published in this direction was by Matthiessen, 1858–1867, who was the first to discover the connection between the electrical conductivity and the constitution of alloys. He divided alloys into four groups, each of which gives a different type of curve on plotting composition in volume concentrations and conductivity. With certain slight alterations, most of Matthiessen's work still holds good, and Guertler<sup>2</sup> has recently given an excellent résumé of the present position of knowledge on this subject.

The following are the particulars of the groups of alloys mentioned above. For the constitution of alloys see p. 225.

**Group I.**—To this group belong those alloys of metals which show only a slight solid solubility in one another. In this case the electrical conductivity is a linear function of the volume concentration of the two metals, and therefore the curve obtained is a straight line. Fig. 32 shows several examples of these alloys, and to this group belong the alloys of Sn–Zn, Sn–Pb, Sn–Cd, Pb–Cd, Zn–Cd, etc.

**Group II.**—To this group belong those alloys which form a

<sup>1</sup> *Accad. Lincei Atti*, xvi, p. 185, Aug. 4, 1907.

<sup>2</sup> *Zeitsch. anorg. Chem.*, li., 4, p. 397; also liv., 1, p. 58.

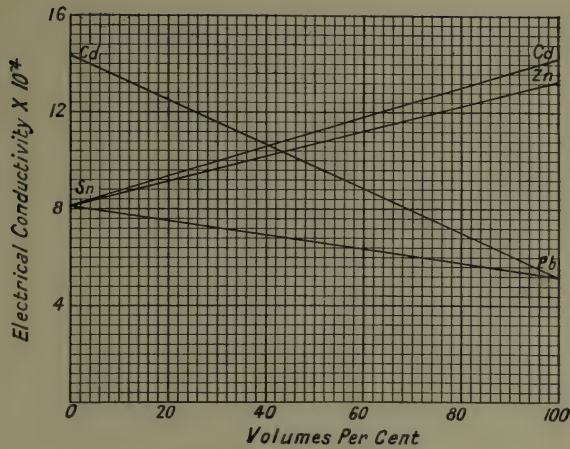


FIG. 32.—Group I., Alloys.

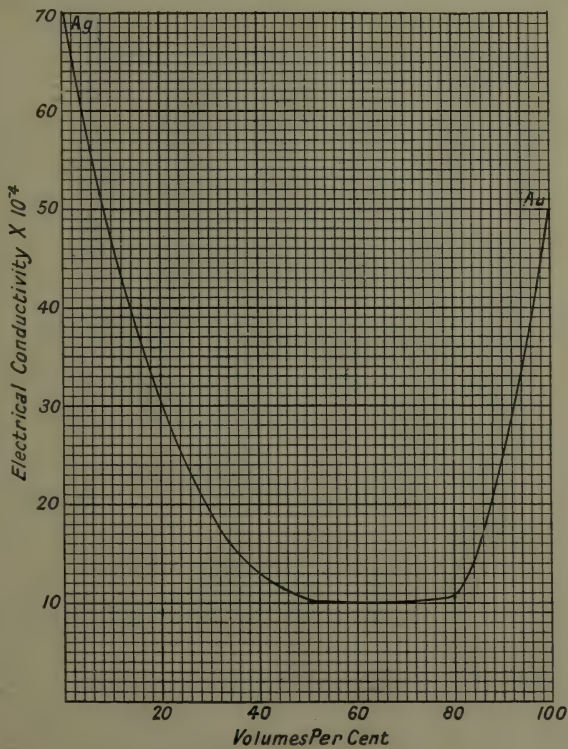


FIG. 33.—Group II., Alloys.



continuous series of mixed crystals, or which are completely soluble in the solid state, forming solid solutions.

In this case the curve obtained is U-shaped, the conductivity being greatly reduced by the addition of successive small amounts of each metal in the other, a low minimum being obtained on a smooth curve. This group comprises the Ag-Au, Ni-Cu, Co-Ni alloys, and the curves obtained are illustrated by fig. 33.

*Group III.*—To this group belong the alloys of metals which

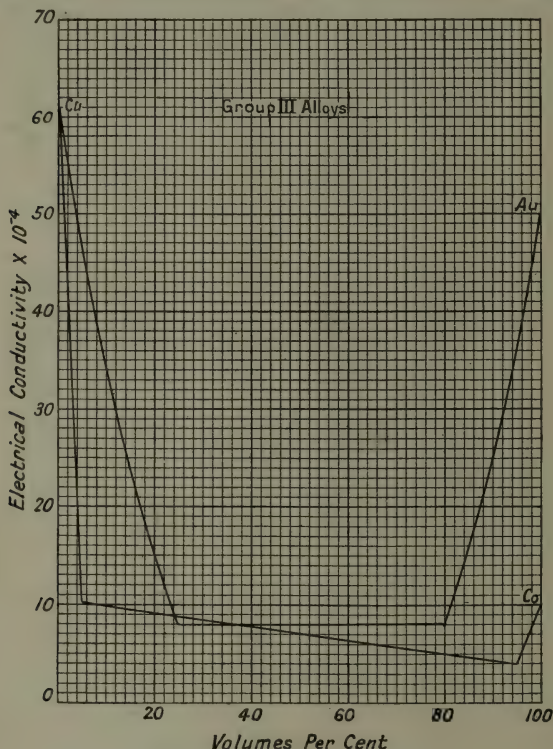


FIG. 34.—Group III., Alloys.

are only partially soluble in the solid state, and which form eutectics (see p. 232) of saturated crystals in the centre of the series.

These alloys give curves which consist of a combination of Groups I. and II., the centre eutectiferous portions give a straight line, and the ends, consisting of solid solutions, show a rapidly decreasing conductivity. To this group belong the alloys Cu-Au, Cu-Ag, Cu-Co, Sn-Bi, Pb-Bi, Au-Bi, etc. Fig. 34 shows the general form of curves obtained.



*Group IV.*—To this group belong the alloys of metals which combine in certain proportions to form true compounds. The curves show maxima or minima points at the places indicated by these compounds. In a series containing  $m$  compounds, the curve may be divided into  $m + 1$  divisions, each of which will be similar to the types given by groups 1, 2, or 3, according to the nature of the constituents. Fig. 35 illustrates this group, and to it belong the alloys Au-Sn, Au-Pb, Sn-Sb, etc.

From published work on the conductivity of alloys, it is found that in no system can the conductivity be higher than that represented by the straight line joining the conductivities of the

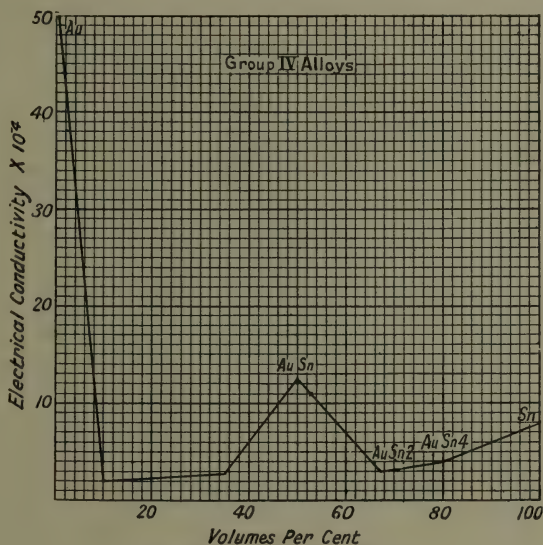


FIG. 35.—Group IV., Alloys.

component metals. Although compounds in alloys do not always show sharp changes of direction in conductivity curves, yet these changes when present always indicate the presence of compounds, sometimes by maximum points, as in the case of  $\text{Cu}_2\text{Sn}$ ,  $\text{AuSn}$ ,  $\text{Cu}_2\text{Sb}$ , etc., or sometimes by minimum points as in  $\text{Cu}_4\text{Sn}$ ,  $\text{Cu}_3\text{Sb}$ ,  $\text{AuSn}_2$ ,  $\text{AuSn}_4$ , etc.

**Influence of Foreign Elements on the Properties of Metals.**—The influence of chemical composition on the mechanical properties of metallic masses is of great importance; this has long been recognised, but it is singular that the subject has been so little investigated. Turn, for instance, to Dr Percy's classical work on Iron and Steel, published in 1864. It fully represents the information which had been gained at that time, yet it con-

tains the results of but few mechanical tests on the materials with which it deals.

The influence of foreign elements is best shown in the case of iron. The properties of this metal are absolutely changed by the presence of a few tenths per cent. of carbon, and the simultaneous presence of other elements greatly complicates these changes.

It seems that metallurgists have only comparatively recently realised that the effect of elements in the presence of each other is very complicated, and that it is absolutely necessary to study the effect of any given element on an absolutely pure mass of the metal to be tested. With regard to iron, the author has shown<sup>1</sup> that the tensile strength of electro-deposited iron, which is as pure as any iron can be, is 2·7 tons per square inch before annealing, and 15·5 tons per square inch after annealing. Even in this case, however, it is doubtful how far the result is influenced by the presence of occluded hydrogen, or by the fact that electrolytic iron is probably an allotropic form of the metal. In studying the effect of carbon, it is very difficult, therefore, to start from pure iron as an absolute basis. One of the most important effects obtained by the addition of carbon to iron is the power of hardening when quenched from a full red heat in water, the hardness thus induced increasing with the percentage of carbon present from ·2 per cent. to about 1 per cent. The degree of hardness conferred is also influenced by the temperature from which the metal is quenched and by the rapidity of quenching. The influence of different percentages of carbon on the tensile strength, elongation, and hardness of steels has been studied by many metallurgists, including Howe, Arnold, Harbord, Wahlberg, and others.

Professor Arnold<sup>2</sup> determined the effect of increasing quantities of carbon by means of a set of extremely pure steels-containing from ·08 to 1·47 per cent. of carbon in the normal condition, that is, heated to 1000° C. and cooled in air, and also in an annealed condition, that is, after heating to 1000° C. for 72 hours and allowing to cool down in the furnace. Fig. 36 is deduced from the results obtained with normal bars, and shows the influence of carbon on the tenacity and ductility of steels. It will be seen that the strength of pure carbon steels will vary from about 19 tons in the case of ·08 carbon steel to about 53 tons with 1 per cent. carbon, the actual figure varying with the heat treatment received; with more than 1 per cent. carbon, the steels generally show a decrease in tensile strength. The elongation is found to gradually decrease as the carbon increases from about 45 per cent. in ·08 carbon steel to about 3 or 4 per cent. in the case of 1·5 carbon steel.

The important point brought out by these researches was

<sup>1</sup> *Journ. Iron and Steel Inst.*, No. i. (1887), p. 74.

<sup>2</sup> *Proc. Inst. Civil Engineers*, cxxiii., 1895-96.

that the saturation point of carbon in steel occurs at about 0.9 per cent. carbon, a point closely associated with many of the important properties of steel.

The effect of carbon on the hardness of steels has been studied by Wahlberg,<sup>1</sup> who shows that the hardness, when quenched in water, gives Brinell number 149 for 0.1 carbon steel and increases to number 627 for 0.92 carbon steel. Unfortunately, the steels used for these tests were not uniform, as they contained varying amounts of silicon and manganese.

The influence of manganese on the properties of steels is of the utmost importance, and the effects produced by its addition vary considerably with the amount added and also with the percentage of carbon present. The general tendency of manganese is to increase the tensile strength and to reduce the ductility. Axle and tyre steels usually contain up to 1 per cent. of manganese,

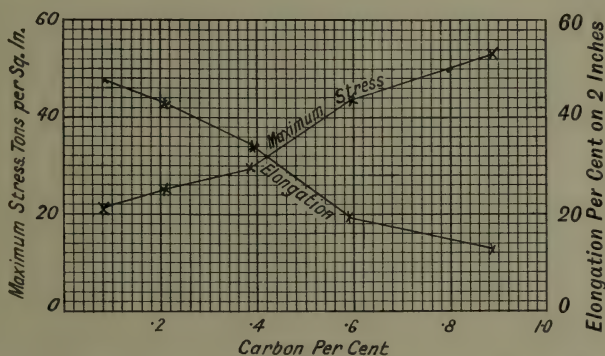


FIG. 33.—Influence of Carbon on the Tenacity and Ductility of Steels.

but in the case of mild steel for boiler plates and for general structural work over 0.6 per cent. begins to be dangerous. The influence of manganese on high carbon tool steels is much more marked, and is usually kept below 0.3 per cent.; when present in greater quantities than this, it is liable to cause fracture on quenching. The foregoing remarks with regard to the action of manganese in the presence of carbon are only true with amounts of manganese not exceeding 2 per cent. Further additions of manganese give remarkable results. Although steel containing from 5.75 to 7 per cent. of manganese, and less than 0.5 per cent. of carbon, is brittle, yet by adding twice this amount of manganese a return in strength is effected; and Hadfield<sup>2</sup> thus obtained the remarkable substance known as manganese steel.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1901, i. p. 267.

<sup>2</sup> *Ibid.*, 1888, ii. p. 41. This contains an excellent bibliography of the subject.



With from 8 to 20 per cent., a cast bar  $2\frac{1}{2}$  inches square can be bent considerably out of the straight without breaking. The increase in strength continues up to about 15 per cent., when a decrease takes place in actual toughness, though not in transverse strength, and after about 20 per cent. is passed a rapid decrease again takes place. Manganese steel, of the best composition, is free from blowholes, and rolls and forges well; but it is so very hard that it is extremely difficult to work in the cold. Its electrical resistance is thirty times that of copper, and eight times that of wrought iron, and for practical purposes it may be regarded as wholly unmagnetisable.

It is very difficult to estimate the influence of **silicon**. It is known that the addition of silicon to molten steel is useful, as it prevents the formation of "blowholes" in the solidifying mass. Probably the silicon acts by *increasing* the solubility of gas in iron until the metal has actually set.

In the case of mild steel there is practically no increase in maximum stress or in the elastic limit until over .4 per cent. of silicon is present; when over this amount, however, there is a tendency for silicon to increase the maximum stress and to reduce the extensibility, especially when 1.5 to 2 per cent. is exceeded.

The results of an elaborate series of mechanical tests by R. A. Hadfield<sup>1</sup> on silicon steel in its forged state gave results which showed that silicon, up to 1.5 or 1.75 per cent., added to iron, although increasing the elastic strength and raising the tensile strength, does not impair ductility. After this, however, the further increase of tensile strength noticed is only obtained with a serious loss of ductility. There appears to be no sharp line of demarcation, but when 1.5 to 2 per cent. is exceeded, further slight increases cause great changes in the characteristics of the material. In this respect, therefore, its action rather resembles that of carbon than that of manganese, of which larger amounts are required to effect similar changes.

For many years it had been recognised by metallurgists that silicon added to finished charges had a different effect on the physical properties of steel from that left in the charge, as it sometimes is, at the end of the Bessemer blow; high silicon steel has been regularly made in the open hearth for tyres and axles, and gives excellent results up to .35 per cent. silicon. Bessemer steel, on the other hand, which contains high silicon, left in the metal at the end of the blow, due to the pig-iron blowing too hot, has been found to be quite unreliable, not probably on account of silicon present, but because of the high temperature developed during the process, of which the presence of silicon is only an indication.

C. P. Sandberg<sup>2</sup> has experimented with silicon in rail steels,

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1889, ii. p. 232.

<sup>2</sup> *Trans. Inst. Civil Eng. Conference*, section i. p. 6.



with a view to obtaining soundness and solidity without brittleness, and has found that for rail steel the effect of silicon added is very different from the effect of silicon left in from pig-iron. When silicon is left in, the percentage varies considerably, depending on the heat of the charge. When, however, the silicon has been eliminated from the pig-iron as far as possible, and a known quantity of silicon is added in the form of high-percentage silico-spiegel or ferro-silicon, then the percentage of silicon is easily regulated, and the wearing properties of the steel are found to be greatly improved, this being largely due to the more complete removal of gases and oxide from the steel. Sandberg finds that silicon up to .35 per cent. gives very good results.

It should be borne in mind that larger additions of silicon do not cause a return of strength, which is so remarkable in the case of manganese steel. Silicon steel is, moreover, still magnetic with considerable percentages of silicon, and is in this respect unlike both manganese and nickel steels. Hopkinson states that the electrical resistance of silicon steel is about six or seven times that of pure iron, and Hadfield has shown that the influence of silicon closely resembles that of aluminium.

The presence of silicon also facilitates the separation of graphitic carbon from iron. Prof. Turner<sup>1</sup> of Birmingham University has done excellent work by studying the action of silicon on pig-iron and steel, and his results have been conveniently condensed by F. Gautier,<sup>2</sup> from whose paper the diagram (fig. 37) has been adapted. The maximum result obtained on the series of samples for each kind of resistance has been taken as unity, and the ordinates are expressed as fractions of this maximum. The datum line of the diagram would, however, fall below the limits of the page.

The chief point of interest is that in pig-iron the maximum resistance to traction (tensile strength), to bending, and to crushing is attained with proportions of silicon varying between 1.5 and 2 per cent. Metal containing between 2 and 3 per cent. of silicon appears to be softer than the rest of the series, whilst the maximum resistance to crushing stress is attained with less than 1 per cent. of silicon. It should be added that in the samples rich in silicon the carbon was mainly present in the graphitic state. These also contained about 0.3 per cent. of manganese, and a small quantity, about 0.04 per cent., of sulphur.

Wahlberg<sup>3</sup> gives fully the relative effects of carbon, silicon, and manganese on the *hardness* of steel as shown by Brinell's method.

The influence of sulphur on iron and steel is very marked. This element has the effect of making iron red-short and unworkable at a red heat, and of destroying its welding power. The

<sup>1</sup> *Journ. Chem. Soc.*, 1885, pp. 577 and 902.

<sup>2</sup> *Bull. Soc. de l'Ind. Min.*, vol. iii. (1889), p. 91. See also paper read at the Metallurgical Congress, Paris, 1889.

<sup>3</sup> *Journ. Iron and Steel Inst.*, 1901, i. p. 267.

effect of sulphur on steel is most noticeable during rolling, a small percentage causing the ingots or bars to crack at the edges. The amount of sulphur which may be present without being perceptible during rolling or welding varies with the process by

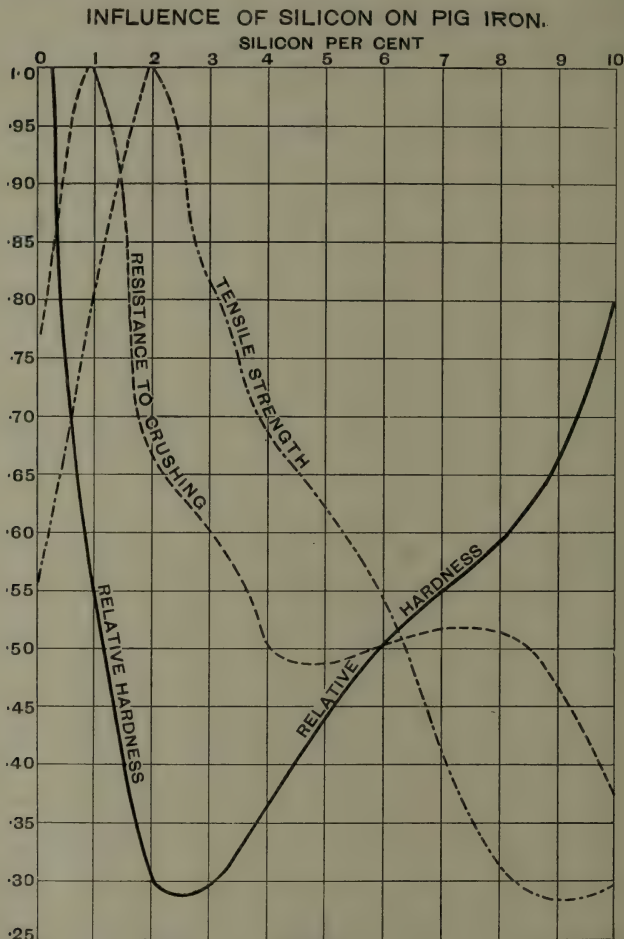


FIG. 37.

which the steel has been made, the amount of manganese and copper present, and the temperature of casting; but for welding and general structural work it should not exceed  $\cdot 06$  per cent., although no signs of red-shortness may be apparent when  $\cdot 1$  is present in certain steels. Manganese counteracts to some extent

the prejudicial action of sulphur, forming with it globules of manganese sulphide, as first shown by Arnold.

Professor Le Chatelier<sup>1</sup> has illustrated this point with some very interesting photomicrographs, which show that sulphur, when present as sulphide of iron, forms a mesh-like structure surrounding the grains of iron, and when manganese is added, these meshes of sulphide are largely broken up, and more or less distributed throughout the mass.

This breaking up of the mesh-work, together with the fact that sulphide of iron has a lower melting-point than the welding temperature of steel, and manganese sulphide has a much higher melting-point than iron sulphide, seem to be a rational explanation of the beneficial effect of manganese in steels containing small amounts of sulphur.

Sulphur is also said to lower the saturation-point of iron for carbon in the molten state, and, like manganese, to prevent to some extent the separation of graphite. Steels containing relatively large percentages of sulphur corrode more rapidly than low sulphur steels.

The influence of phosphorus in steels is most important, and varies considerably with the percentage of carbon present; the higher the carbon, the more prejudicial is the effect of phosphorus, and in the best qualities of crucible tool steels only the very purest materials are used, the phosphorus being frequently under .01 per cent. The most marked effect of phosphorus is the inducement of cold-shortness and brittleness when subjected to suddenly applied stresses, or, in other words, to "shock." The tensile strength, elongation, etc., appear to be very slightly affected by phosphorus, but there is no doubt that the lower the percentage of this element, the safer will the steel be, and in the case of steel for structural purposes, the limit should be .06 per cent., while in rails .08 per cent. may be allowed with safety.

Stead<sup>2</sup> has published very important results on the relation of phosphorus and iron, which should be consulted by the student.

The effect of arsenic in such proportion as is usually present in commercial steels, that is, less than 0.1 per cent., is very little, except with regard to its welding properties. Harbord and Tucker<sup>3</sup> made a series of experiments on the effect of arsenic on mild steel, and came to the conclusion that up to .17 per cent. it had no effect on the ductility or tenacity of the steel. With .25 per cent. the steel could not be welded, but even 1 per cent. produced no red-shortness at rolling temperatures. Stead<sup>4</sup> has also examined the effect of arsenic on steel, and concluded that between .1 and .15 per cent. of arsenic has no effect on the mechanical

<sup>1</sup> *Bulletin de la Société d'Encouragement*, Sept. 1902.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1900, ii. p. 60.

<sup>3</sup> *Ibid.*, 1888, i. p. 183.

<sup>4</sup> *Ibid.*, 1895, i. p. 108.



properties, but that its influence is just noticeable with 0·2 per cent. The rolling and forging properties are not affected by considerable quantities of arsenic, but welding is much more difficult when comparatively small quantities are present.

To take copper as an example instead of iron, the influence of bismuth is most marked, for although it is easily oxidised, yet it clings to copper with much tenacity, and affects its properties in a most surprising manner. Hampe found that ·02 per cent. was sufficient to make the metal distinctly red-short, and cold-shortness begins with ·05 per cent. With 0·1 per cent. Bi the copper crumbles under the hammer at a red heat.

According to Keller,<sup>1</sup> a few thousandths per cent. of bismuth render copper unsuitable for electric conductors.

Sulphur often occurs in unrefined copper and renders the metal cold-short; Hampe found, however, that copper with ·25 per cent. of sulphur was moderately malleable, but with 0·5 per cent. it became very cold-short, though, curiously, such copper was not red-short.

With regard to the effect of antimony on copper, it has been stated that 0·001 per cent. was very injurious, rendering it unfit for the manufacture of brass wire and sheet. Hampe,<sup>2</sup> however, found that metallic copper containing 0·529 per cent. could be drawn into the finest wire; and Brand<sup>3</sup> states that copper containing 0·5 per cent. of antimony can be worked easily into hollow wire. Extreme red-shortness is caused by 1 per cent. of antimony. Small quantities of antimony seriously affect the electrical properties, reducing the conductivity, and Keller<sup>4</sup> states that a few thousandths per cent. render copper unsuitable for conductors.

Taking gold as an example, it may be stated that very small quantities of lead, bismuth, tin, cadmium, antimony, arsenic, tellurium, or zinc render gold brittle. Lead, bismuth, and tin, when present up to ·002 per cent., produce brittleness; and Hatchett states that gold containing ·00032 per cent. of antimony is no longer malleable. Although zinc alone renders gold brittle, yet if there be present at the same time silver and copper, then even 5 to 7 per cent. of zinc does not affect the malleability of the metal.

We will next consider one or two typical instances of the effect of metals in varying quantities on each other, forming what are considered to be true alloys.

**Influence of varying Quantities of Metals on each other.**—The effect of the addition of tin to copper, as far as mechanical

<sup>1</sup> *Mineral Industry*, vol. vii. p. 259.

<sup>2</sup> *Chemiker Ztg.*, 1892, xvi., No. 42.

<sup>3</sup> *Dammer's Chem. Technologie*.

<sup>4</sup> *Trans. Amer. Inst. Min. Eng.*, 1898.



properties are concerned, is shown by the accompanying diagram

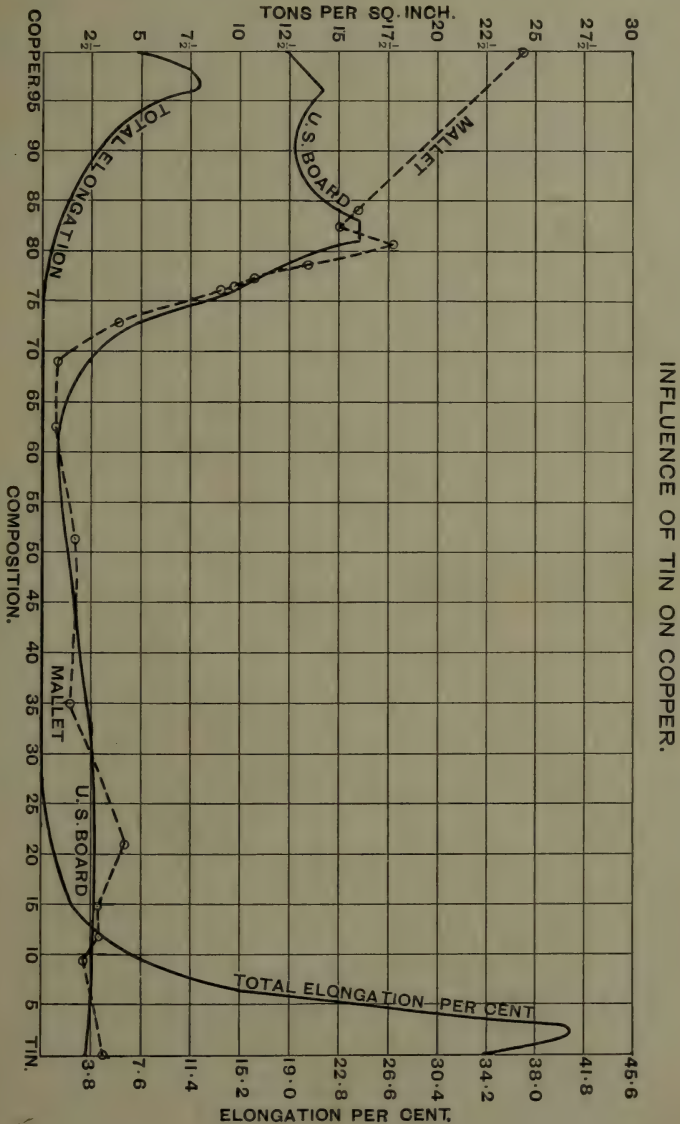


Fig. 38.

(fig. 38), in which the upper curves represent the tensile strengths as determined by Mallet and by a Board of investigators appointed

by the Government of the United States.<sup>1</sup> It may be sufficient to state that the addition of tin to copper rapidly lowers its conductivity for electricity, but, as shown by the results obtained by the U.S. Board, increases its strength, the maximum being attained with about 20 per cent. of tin. An example of the effect of tin on the hardness of copper occurs in the use of bronze for coinage and for metal-work.<sup>2</sup> In the former case the amount of tin is 4 per cent., but if it exceeded 2 per cent. in the latter it would be too hard to give the desired impression. The entire series of copper-tin alloys is very interesting. Two only appear to be homogeneous, and these correspond respectively to the formulæ  $\text{SnCu}_3$  and  $\text{SnCu}_4$ . Notwithstanding the comparatively small difference in their composition, the appearance of the fractured surfaces of these alloys is quite different, the latter being yellowish-grey in colour with a mirror-like fracture, whilst the former is blue with a rough fracture. Having a higher specific gravity than the mean of its constituents, the alloy  $\text{SnCu}_3$  stands out from the rest of the series. Heycock and Neville<sup>3</sup> have shown that a marked difference in properties and microstructure occurs when copper-tin alloys undergo varying thermal treatment.

The influence of aluminium on copper is of great industrial importance, and has been the subject of much research. The Eighth Report to the Alloys Research Committee of the Inst. of Mechanical Engineers<sup>4</sup> contained the results of an elaborate examination of copper aluminium alloys, and should be referred to by the student. Up to 10 per cent. of aluminium there is a gradual increase in the ultimate stress of the alloys, and this point is practically the limit of industrially serviceable alloys, as beyond it there is a rapid fall of ductility and ultimate stress. These alloys may be divided into two classes, the first containing up to 7.35 per cent. Al, with low yield point, moderate ultimate stress, but very good ductility; the second class containing alloys from 7.35 to 10 per cent. Al, with relatively low yield point but good ultimate stress. See fig. 39 for these tests.

The alloys containing from 15 to 90 per cent. of Al do not appear to be of any technical promise. From 15 to 18 per cent. they are very hard, but very brittle. From about 20 to 65 per cent. they diminish in hardness, and are so brittle that they can be powdered with ease in a mortar. Most of them break if dropped on a hard floor. This excessive brittleness ceases at about 67 per cent. Al. Beyond 90 per cent. Al we have another series of useful alloys which really illustrate the influence of

<sup>1</sup> *Report on a Preliminary Investigation of the Properties of the Copper-Tin Alloys*, Washington, 1879.

<sup>2</sup> *Annual Mint Report*, 1901.

<sup>3</sup> *Phil. Trans. Roy. Soc.*, 1901.

<sup>4</sup> *Proc. Inst. Mech. Eng.*, 1907, p. 64.

copper on aluminium, but it is found that nothing is to be gained by the addition of more than 4 per cent. of Cu. This

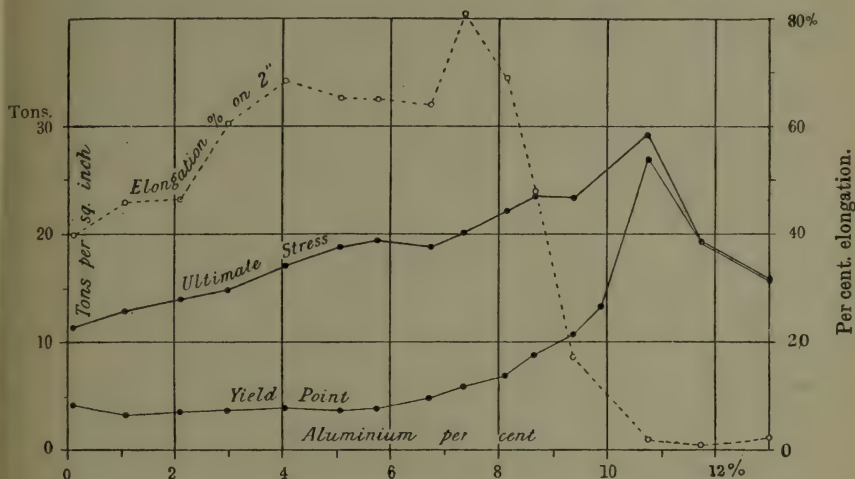


FIG. 39.—Influence of Aluminium on Copper. Tensile Tests on Sand Castings. Slowly cooled from 800° C. (1472° F.).

addition causes a fall of ductility and a rise of tenacity which are fairly steady up to 4 per cent., beyond which there is no

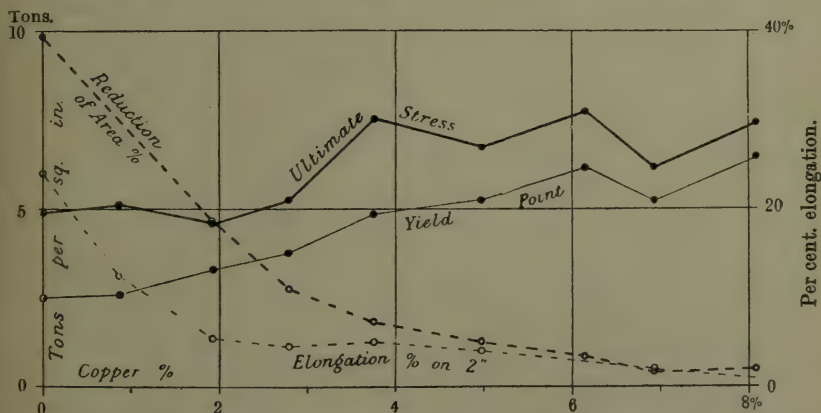


FIG. 40.—Influence of Copper on Aluminium Sand Castings.

increase in tenacity, while the ductility continues to diminish. Fig. 40 will illustrate the general effect of Cu on Al up to 8 per cent.

**Relationship between the Atomic Volume of an Element added to a Metal and the Effect produced by this Addition.—**

In studying this question, it must be borne in mind that any relationship between the atomic volume of an added element and the effect produced by its addition can only hold good in those cases in which solid solutions are formed. There are many instances in which an added element, even in small quantities, causes the formation of a eutectic, which, in turn, greatly reduces the strength of the metal to which it is added, and in these cases there is absolutely no connection between the properties and the atomic volume. Since 1826, when Gmelin called attention to the relation between the atomic weights of elements which have similar properties, chemists have been actively engaged in establishing analogies between the properties of the elements and in arranging them systematically, and the result has been (mainly through the labours of Newlands, Mendeléeff, and Lothar Meyer) the promulgation of the Periodic law. This law states that the properties of the elements are a periodic function of their atomic weights. Lothar Meyer has gone further, and has shown that a remarkable relation exists between the atomic volumes of the elements. Now, however tiny the atoms may be, they must possess volume, and the atomic volume of each element will be peculiar to itself. The space occupied by one atom cannot yet be measured absolutely, but relative measurements may be obtained "by taking such quantities of the elements as are proportional to their atomic weights, and comparing the space occupied by these quantities." The relative atomic volumes of the elements are found by dividing the atomic weights by their specific gravities in the solid state. The atomic weight of gold is 197.2;  $\frac{197.2}{19.3} = 10.2$  the atomic volume, or, expressed in the

metric system, 197.2 grammes of gold would occupy a space of 10.2 cubic centimetres. Lead, on the other hand, would have the large atomic volume of 18.2, and potassium that of 45.5. The question now arises—Does the power to produce fragility, which we have seen certain elements to possess, correspond to any other of their properties by which they may be classified? The facts represented in the Periodic law were, in 1869, graphically represented by Lothar Meyer in his well-known curve of the elements. By adopting atomic weights and atomic volumes as co-ordinates he showed that the elements can be arranged in a curve representing a series of loops, the highest points of which are occupied by caesium, rubidium, potassium, sodium, and lithium, whilst the metals which are most useful for industrial purposes occupy the lower portions of the several loops.

An examination of some results the author<sup>1</sup> obtained shows

<sup>1</sup> *Proc. Roy. Soc.*, vol. xliii. (1888), p. 425; and *Phil. Trans.*, vol. clxxix. (1888), A., p. 339.



that not a single metal or metalloid which occupies a position at the base of either of the loops of Lothar Meyer's curve diminishes the tenacity of gold. On the other hand, the fact is clearly brought out that metals which render gold fragile all occupy high positions on the curve. This would appear to show that there is some relation between the influence exerted by the metallic and other impurities and either their atomic weights or their atomic volumes. It seems hardly probable that it is due to atomic weight, because copper, with an atomic weight of 63.6, has nearly the same influence on the tenacity of pure gold as rhodium, with an atomic weight of 103.

Several of the elements, the action of which was examined, occupy abnormal positions, and one reason for this is that solid solutions are not formed in these cases. It is difficult to offer any mechanical theory to account for the action of the elements, but it may perhaps be well to give a rough indication of what may take place. If five spheres, representing atoms of a certain volume, are arranged in one plane so as to touch each other, then the addition of an element with a small atomic volume may improve the tenacity by filling up the central space which would otherwise remain void; with such an arrangement of five atoms the addition of an element with the same atomic volume as themselves will tend to drive them slightly further asunder, and should, therefore, act prejudicially in a five-atom group, although it would exactly fill the space between a six-atom group, but in either case the insertion of a larger atomic volume than that of each member of the group must tend to drive the members of either the five- or six-atom group further asunder, and by so doing would diminish the cohesion of the mass.

It is, however, inadvisable in the present state of our knowledge to formulate any definite law on the relation between the atomic volume and the physical properties produced by alloying one element with another, and much research work remains to be done before it will be wise to generalise in this direction.

**Effect of Temperature on Strength of Alloys.**—With reference to the strength of alloys at different temperatures, Prof. Unwin<sup>1</sup> observes that, in the case of commonly used alloys, such as gun-metal and brass, the question is one of practical importance. Some experiments made by him in 1877 for the Admiralty proved that Muntz-metal and phosphor-bronze showed a fairly regular decrease in tenacity, as the temperature was raised to 260°, and in the case of gun-metal the tenacity diminished *regularly* up to a temperature of 150° to 175°, while beyond that temperature there was a *sudden* decrease of tenacity, generally of more than 50 per cent., and in several cases at a temperature of 260° the tenacity had very greatly decreased. This is important, because at the high pressures and correspondingly high temperatures at which

<sup>1</sup> *Report Brit. Assoc.*, 1889, p. 746.

steam engines are often worked, gun-metal may be exposed to temperatures of  $175^{\circ}$  to  $230^{\circ}$ ; and in order to ascertain whether at such temperatures the strength of such alloys is seriously impaired, Prof. Unwin has made a further series of experiments.

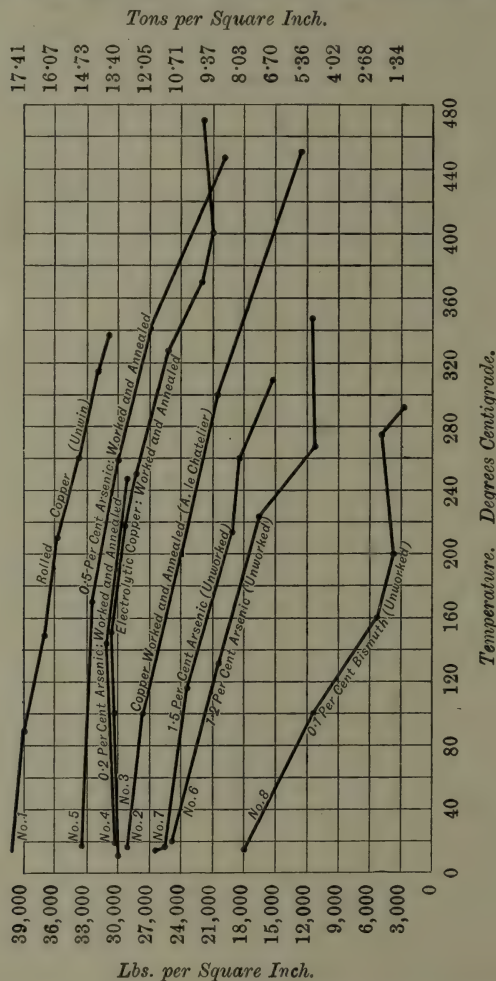


FIG. 41.—Tensile Strength of Copper Rods.

The results showed that with yellow-brass, Muntz-metal, and Delta-metal the decrease of tenacity follows a regular law without any sudden loss of strength. Even at temperatures of  $315^{\circ}$  to  $345^{\circ}$  all the bars had a not inconsiderable tenacity. The ultimate elongation of the bars was measured, and a peculiarity

in the influence of temperature was observed. In most cases the ultimate elongation diminishes with increase of temperature. With Muntz-metal the decrease is regular, and there is still a considerable elongation before fracture at temperatures above  $340^{\circ}$ . With yellow-brass the decrease is more rapid, and there is very little elongation before fracture at temperatures above  $260^{\circ}$ . The elongations of the gun-metal bars were very irregular, and at temperatures of over  $260^{\circ}$  the elongations were but small. On the other hand, in the case of Delta-metal bars, the elongation increased regularly with the increase of temperature.

The preceding series of curves (fig. 41) shows the results obtained with copper of varying degrees of purity at temperatures ranging between  $15^{\circ}$  C. and  $470^{\circ}$ . It will be observed that the effect of bismuth is very noteworthy.<sup>1</sup>

A number of determinations have been made of the strength of aluminium-copper alloys at high temperatures, and some of these will be found in the Eighth Report to the Alloys Research Committee,<sup>2</sup> where the method of heating electrically during the testing is also described. The following results are the mean figures obtained for two alloys at the temperatures given:—

Temperature.	Ultimate Stress. Tons per Sq. In.	
	Cu 90·06 per cent.; Al 9·9 per cent.	Cu 93·23 per cent.; Al 6·73 per cent.
Ordinary . . . . .	38·1	28·8
$200^{\circ}$ C. . . . .	36·4	
$300^{\circ}$ C. . . . .	33·4	20·7
$400^{\circ}$ C. . . . .	24·0	17·9
$500^{\circ}$ C. . . . .	12·1	10·9
$550^{\circ}$ C. . . . .	9·1	

It will thus be seen that with rise of temperature there is a gradual decrease of tenacity, the alloy containing 9·9 per cent. Al becoming rapidly weaker at  $450^{\circ}$ ; the loss of tenacity in this case was accompanied by a rise in ductility up to  $500^{\circ}$ , whereas in the alloy containing 6·73 per cent. Al the decrease of tenacity was also accompanied by a gradual decrease of ductility.

#### The Effect of Low Temperatures on the Properties of Alloys.

—The effect of low temperatures on the properties of metals was given on p. 25, and it will now be shown that the effect on alloys is very similar, the tenacity of all the common alloys being increased at low temperatures. Solder and fusible metal, for

<sup>1</sup> *Proc. Inst. Mech. Eng.*, 1893, p. 102.

<sup>2</sup> *Ibid.*, 1907, p. 290.



instance, stretch less, and the cross section of the break is much less at  $-182^{\circ}$  than at ordinary temperatures.

Sir James Dewar illustrated the profound changes which take place in the elastic constants of a metallic body by comparing the deflection produced on a rod of fusible metal by means of a weight at different temperatures; the Young's modulus was found to be between four and five times as great at the temperature of liquid air as at the ordinary temperature. He also showed by experiments on a spiral spring made of fusible metal that the rigidity of metals was greatly changed. At ordinary temperatures an ounce weight was sufficient to draw the spring into a straight wire, whereas the same spring supported a two-pound weight and vibrated like a steel spring at  $-182^{\circ}$ .

Hadfield<sup>1</sup> showed that with nickel steels low in carbon the effect of the liquid air is to double the tenacity, but the ductility is not reduced to the same extent as with most steels. This is an important fact, and proves that the brittleness of iron at low temperatures can be modified by another element, such as nickel. In a steel, however, containing 12 per cent. of nickel and 0.97 per cent. of carbon, there was no change in tenacity or ductility at low temperature.

In manganese steels the results are similar, there being either an increase in tenacity and a decrease in ductility, or else no change at all, depending on the amount of manganese and carbon present. An important point brought out by the experiments on manganese steels is, that at no range of increase or decrease of temperature does any change in magnetic properties occur unless the carbon present is given time to dissociate by many days' continued heating.

In steels containing nickel, manganese, and carbon the effect of liquid air varies considerably, according to the percentage of the various elements present. A specimen containing C 0.60, Mn 5.04, Ni 14.55 per cent. showed remarkable results; for whereas the nickel and manganese added separately to iron in these proportions would cause intense brittleness, the double combination confers extraordinary toughness. This specimen also remained practically non-magnetic at temperatures high and low, and it is useful to remember here that nickel steels containing about 20 per cent. Ni, which are non-magnetic at ordinary temperatures, become magnetic at  $-180^{\circ}$  C., and again lose this property on heating. Another interesting alloy contained C 1.18, Mn 6.05, Ni 24.3 per cent.; it was the first specimen met with which showed an increase of tenacity from 51 to 84 tons, and also an increase of ductility from 60 to 67 per cent.

The alloys containing 6 per cent. of manganese and 14 to 24 per cent. of nickel show remarkable toughness and ductility, are almost non-magnetic, and possess a very high electrical resistance.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1905, i. p. 147.



**The Rarer Metals and their Alloys.**—With the exception of platinum, the rarer metals are little used except when alloyed, and it may be well, therefore, to show how the rarer metals may be isolated, and to indicate the nature of the influence they exert. With the exception of the action of carbon upon iron, probably nothing is more remarkable than the action of the rare metals on steels; but their peculiar influence often involves the presence of carbon in the alloy.

The metals which, for the purposes of this book, may be included among the rarer metals, are (1) those of the platinum group, which occur in nature in the metallic state; and (2) certain metals which in nature are usually found as oxides or in an oxidised form of some kind, such as chromium, manganese, vanadium, tungsten, titanium, tantalum, zirconium, uranium, and molybdenum (which occurs as sulphide). Incidental reference will be made to nickel and cobalt.

As regards the rarer metals which are associated with oxygen, the problem is to remove the oxygen, and this is usually effected either by affording the oxygen an opportunity for uniting with another metal, or by reducing the oxide of the rare metal by carbon, aided by the dissociating effect of an electric current. When an intimate mixture, in atomic proportions of oxide of chromium and finely divided metallic aluminium, is heated locally to a temperature of  $1010^{\circ}$ , energetic action takes place; the temperature suddenly rises above the melting-point of platinum, and when cold, if the crucible be broken open, it will be seen that a mass of metallic chromium has been liberated.

The use of alkaline metals in separating oxygen from other metals is well known. Its history is associated with the honoured names of Berzelius, Wöhler, and Winkler.<sup>1</sup> The industrial importance of this method of reduction as the result of experimental work was dealt with in a lecture by the author.<sup>2</sup>

Mr Vautin has shown that granulated aluminium may readily be prepared, and that it renders great service when employed as a reducing agent; and his assistant, Mr Picard, who was formerly a student at the Royal School of Mines, isolated certain specimens of rare metals in the laboratory at the Mint.

The relation of aluminium to other metals is very singular. When, for instance, a small quantity of aluminium is present in cast iron, it protects the silicon, manganese, and carbon from oxidation.<sup>3</sup> The presence of silicon in aluminium greatly adds to the brilliancy with which aluminium itself oxidises and burns. It is also known that aluminium, even in small quantity, exerts

<sup>1</sup> An interesting paper by H. F. Keller, on the reduction of oxides of metals by other metals, will be found in the *Journal of the American Chemical Society*, December 1894, p. 833.

<sup>2</sup> *Nature*, Aug. 8, 1901.

<sup>3</sup> *Bull. Soc. Chim. Paris*, vol. xi., 1894, p. 377.

a powerful protective action against the oxidation of the silver zinc alloy, arising from the desilverisation of lead by zinc.

Moreover, if a mass of aluminium be heated to redness in air, the film of oxide which is formed will protect the mass from further oxidation.<sup>1</sup> On the other hand, if finely divided aluminium finds itself in the presence of an oxide of a rare metal at an elevated temperature, it at once acts with energy and promptitude, and releases the rare metal from the bondage of oxidation. Aluminium, moreover, retains the oxygen it has acquired with great fidelity, and will only part with it again by electrolytic action, or at very high temperatures under the influence of the electric arc in the presence of carbon.

If a suitable mixture of red-lead and aluminium be placed in a small crucible heated in a wind furnace, in two minutes an explosion will announce the termination of the experiment. The crucible will be shattered to fragments.

It is admitted that a metal will abstract oxygen from another metal if the reaction is more exothermic than that by which the oxide to be decomposed was originally formed. The heat of formation of alumina is 391 calories, that of oxide of lead is 51 calories; so that it might be expected that metallic aluminium, at an elevated temperature, would readily reduce oxide of lead to the metallic state.

The experiment just referred to proved that the reduction of oxide of lead by aluminium is effected with explosive violence, the temperature engendered by the reduction being sufficiently high to volatilise the lead. Other experiments show that the explosion takes place with much disruptive power when aluminium reacts on oxide of lead *in vacuo*, and that if coarsely-ground fused litharge be substituted for red-lead, the action is only accompanied by a rushing sound. The result is, therefore, much influenced by the rapidity with which the reaction can be transmitted throughout the mass. It is this kind of experiment which makes us turn with such vivid interest to the teaching of the school of St Claire Deville, the members of which have rendered such splendid services to physics and metallurgy. They do not advocate the employment of the mechanism of molecules and atoms in dealing with mechanical problems, but would simply accumulate evidence as to the physical circumstances under which chemical combination and dissociation take place, viewing these as belonging to the same class of phenomena as solidification, fusion, condensation, and evaporation. They do not even insist upon the view that matter is minutely granular, but in all cases of change of state make calculations on the basis of work done, viewing changed "internal energy" as a quantity which should reappear when the system returns to the initial state.

A verse, of some historical interest, may appeal to them. It

<sup>1</sup> *Zeitschr. Electrochem.*, xiv. p. 766, Nov. 30, 1908.

occurs in a thirteenth-century poem of the period, that is, the *Roman de la Rose*, and it expresses Nature's protest against those who attempt to imitate her works by the use of mechanical methods. The "argument" runs thus:

"Comme Nature se complaint,  
Et dit sa douleur et son plaint  
A ung sot souffleur sophistique  
Qui n'use que d'art mécanique."

If the "use of mechanical art" includes the study of chemistry on the basis of the mechanics of the atoms, the modern school may be offered the following rendering of Nature's plaint:

"How Nature sighs without restraint,  
And grieving makes her sad complaint  
Against the subtle sophistry  
Which trust atomic theory."

An explosion such as is produced when aluminium and oxide of lead are heated in presence of each other, which suggested the reference to the old French verse, does not often occur, as in most cases the reduction of the rarer metals by aluminium is effected quietly.

Vanadium and uranium may readily be reduced from their oxides by means of aluminium, as well as manganese, tungsten, and titanium. Allusion will be made subsequently to the uses of these metals. Some properties of titanium are of special interest. It burns with brilliant sparks in air, and it appears to be, from the experiments of M. Moissan, the most difficultly fusible metal known; but it has the singular property of burning in nitrogen—it presents, in fact, the only known instance of vivid combustion in nitrogen. Lord Rayleigh has recently stated that titanium does not combine with argon; and M. Guntz points out that lithium in combining with nitrogen produces incandescence. M. Moissan has also shown that uranium does not absorb argon.

**Electrolytic Fusion.**—The other method by which the rarer metals may be isolated is that which involves the use of the electric furnace. In this connection the name of Sir W. Siemens should not be forgotten. He described the use of the electric arc furnace in which the carbons were arranged vertically, the lower carbon being replaced by a carbon crucible; and in 1882 he melted in such a furnace no less than ten pounds of platinum. It may fairly be claimed that the large furnaces with a vertical carbon, in which the bath is maintained fluid by means of the electric current, the aluminium and other metals being reduced by electrolytic action, are the direct outcome of the work of Siemens.

In the development of the use of the electric arc for the isolation of the rare, difficultly fusible metals, Moissan stands in the



front rank. He points out<sup>1</sup> that Despretz<sup>2</sup> used in 1849 the heat produced by the arc of a powerful pile; but Moissan was the first to employ the arc in such a way as to separate its heating effect from the electrolytic action it exerts. This he did by placing the poles in a horizontal position, and by reflecting their heat into a receptacle below them. He has shown, in a series of classical researches, that employing 800 amperes and 110 volts a temperature of at least  $3500^{\circ}$  may be attained, and that many metallic oxides which until recently were supposed to be irreducible may be readily made to yield the metal they contain.<sup>3</sup>

A support or base for the metal to be reduced is needed, and this is afforded by magnesia, which appears to be absolutely stable

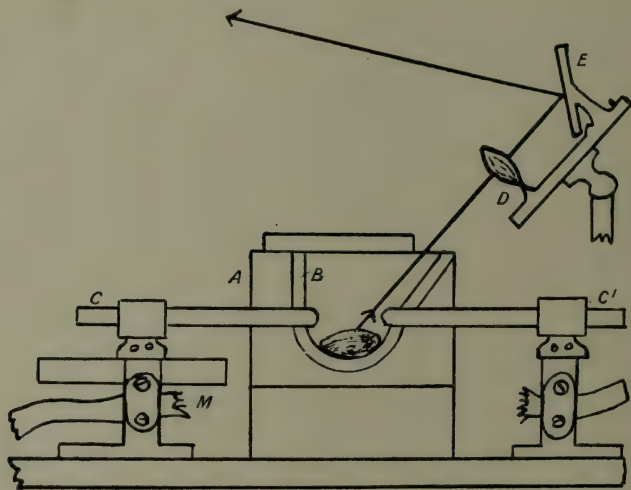


FIG. 42.

at the utmost temperatures of the arc. An atmosphere of hydrogen may be employed to avoid oxidation of the reduced metal, which, if it is not a volatile one, remains at the bottom of the crucible, almost always associated with carbon—forming, in fact, a carbide of the metal. As an illustration of the way in which the furnace is used the following experiment may be described.

The furnace (fig. 42) consists of a clay receptacle A, lined with magnesia B. A current of 60 amperes at 100 volts is introduced by the carbon poles C C'; an electro-magnet M is provided to deflect the arc on to the metal to be melted. By means of a

<sup>1</sup> *Ann. de Chim. et de Phys.*, vol. iv., 1895, p. 365.

<sup>2</sup> *Comptes Rendus*, vol. xxviii. p. 755, and vol. xxix., 1849, pp. 48, 545, 712.

<sup>3</sup> See *Le Four Électrique*, Paris, 1897; English translation, 1904.



lens and mirror DE the image of the arc and of the molten metal may be projected on to a screen. For this purpose it is found convenient to make the furnace much deeper than would ordinarily be the case.

The result is very beautiful, and when arranged for the melting of metallic chromium, directly the current is passed the picture reflected by the mirror E (fig. 42) shows the interior of the furnace as a dark crater, the dull red poles revealing the metallic lustre and grey shadows of the metal beneath them. A little later these poles become tipped with dazzling white, and in the course of a few minutes the temperature rises to about  $2500^{\circ}$  C. Such a temperature will keep chromium well melted, though a thousand degrees more may readily be attained in a furnace of this kind. Each pole is soon surrounded with a lambent halo of the green-blue hue of the sunset, the central band of the arc changing rapidly from peach-blossom to lavender and purple. The arc can then be lengthened, and as the poles are drawn further and further asunder the irregular masses of chromium fuse in silver droplets below an intense blue field of light, passing into green of lustrous emerald; then the last fragments of chromium melt into a shining lake, which reflects the glowing poles in a glory of green and gold, shot with orange hues. Still a few minutes later, as the chromium burns, a shower of brilliant sparks of metal are projected from the furnace amid the clouds of russet or brown vapours which wreath the little crater; whilst, if the current is broken and the light dies out, you wish that Turner had painted the limpid tints, and that Ruskin might describe their loveliness.

The effect when either tungsten or silver replaces chromium is much the same, but in the latter case the glowing lake is more brilliant in its turbulent boiling, and blue vapours rise to be condensed in the iridescent beads of distilled silver which stud the crater walls.

It must not be forgotten that the use of the electric arc between carbon poles renders it practically impossible to prepare the rare metals without associating them with carbon, often forming true carbides; and it is impossible in many cases to separate the carbon by subsequent treatment. Moissan has, however, opened up a vast field of industrial work by placing at our disposal practically all the rarer infusible metals which may be reduced from oxides, and it is necessary for us now to consider how we may best enter upon our inheritance. Those members of the group which we have known long enough to appreciate are chromium, manganese, tungsten, vanadium, and molybdenum, and these we have only known free from carbon for a few years.

The question naturally arises—Why do small quantities of these rarer metals either increase or diminish the strength of masses of metals to which they are added? The answer would appear to

be as follows: Most alloys have more than one solidifying point. Sometimes, if the added element forms a possible alloy with the metal which constitutes the mass in which it is hidden, the second or even the third solidifying point will be low in the scale of temperature. If the subordinate point is low, the metal will be weak; if it is high in relation to the main setting point, then the metal will be strong. The rarer metals which demand for their isolation from their oxides either the use of aluminium or the electric arc, appear not to produce low freezing-points when they are added in small quantities to those metals which are used for constructive purposes. How these rarer metals act, why the small quantities of the added rare metals strengthen the metallic mass, we do not know; we are only gradually accumulating evidence which is afforded by very delicate methods of investigation.

**The Industrial Use of the Rarer Metals.**—It may be well to point to a few instances in which the industrial use of such of the rarer metals as have been available in sufficient quantity is made evident. Modern developments in armour-plate and projectiles will occur to many of us at once, and the effect of projectiles of approximately the same weight, when fired with the same velocity against 6-inch plates, enables comparative results to be studied, and illustrates the fact that the rivalry between artillerists who design guns, and metallurgists who attempt to produce both impenetrable armour-plates and irresistible projectiles, forms one of the most interesting pages in our national history. When metallic armour was first applied to the sides of war vessels, it was of wrought iron, and proved to be of very great service by absolutely preventing the passage of ordinary cast-iron shot into the interior of the vessel, as was demonstrated through the American Civil War in 1866. It was found to be necessary, in order to pierce the plates, to employ harder and larger projectiles than those then in use, and the chilled cast-iron shot with which Colonel Palliser's name is identified proved to be formidable and effective. The point of such a projectile was sufficiently hard to retain its form under impact with the plate, and it was only necessary to impart a moderate velocity to a shot to enable it to pass through the wrought-iron armour.

It soon became evident that in order to resist the attack of such projectiles with a plate of any reasonable thickness, it would be necessary to make the plate harder, so that the point of the projectile should be damaged at the moment of first contact, and the reaction to the blow distributed over a considerable area of the plate. This object could be obtained by either using a steel plate, in a more or less hardened condition, or by employing a plate with a very hard face of steel, and a less hard but tougher back. The authorities in this country during the decade 1880-90 had a very high opinion of plates that resisted attack without the

development of through-cracks, and this led to the production of the compound plate. The backs of these plates are of wrought iron, the fronts are of a more or less hard variety of steel, either cast on, or welded on by a layer of steel of an intermediate quality cast between the two plates. Armour-plates of this kind differ in detail, but the principle of their construction is now generally accepted as correct.

Such plates resisted the attack of large Palliser shells admirably, as when such shells struck the plate they were damaged at their points, and the remainder of the shell was unable to perforate the armour against which it was directed. An increase in the size of the projectiles led, however, to a decrease in the resisting power of the plates, portions of the hard face of which would at times be detached in flakes from the junction of the steel and the iron. An increase in the toughness of the projectiles by a substitution of forged chrome-steel for chilled iron secured a victory for the shot, which was then enabled to impart its energy to the plate faster than the surface of the plate itself could transmit the energy to the back. The result was that the plate was overcome, as it were, piecemeal; the steel surface was not sufficient to resist the blow itself, and was shattered, leaving the projectile an easy victory over the soft back. It must not be forgotten, in this connection, that the armour of a ship is but little likely to be struck by heavy projectiles in the same place, although it might be by smaller ones.

Plates made entirely of steel, on the other hand, were found, prior to 1888, to have a considerable tendency to break up completely when struck by the shot. It was not possible, on that account, to make their faces as hard as compound plates; but while they did not resist the Palliser shot nearly as well as the rival compound plate, they offered more effective resistance to steel. It appears that Berthier recognised, in 1820, the great value of chromium when alloyed with iron; but its use for projectiles, although now general, is of comparatively recent date, and these projectiles now commonly contain from 1.2 to 1.5 per cent. of chromium, and will hold together even when they strike steel plates at a velocity of 2000 feet per second;<sup>1</sup> and unless the armour-plate is of considerable thickness, such projectiles will even carry bursting charges of explosives through it.

It now remained to be seen what could be done in the way of toughening and hardening the plates so as to resist the chrome-steel shot. About the year 1888 very great improvements were made in the production of steel plates. Devices for hardening and tempering plates were ultimately obtained, so that the latter were hard enough throughout their substance to give them the necessary resisting power without such serious cracking as had occurred in previous ones. In 1889 Mr Riley exhibited, at

<sup>1</sup> *Journal U.S. Artillery*, 1893, vol. ii. p. 497.



the meeting of the Iron and Steel Institute, a thin plate that owed its remarkable toughness to the presence of nickel in the steel. The immediate result of this was that plates could be made to contain more carbon, and hence be harder, without at the same time having increased brittleness; such plates, indeed, could be water-hardened and yet not crack.

For hardening, Éverard had developed the use of the lead bath in France, while Captain Tressider<sup>1</sup> had perfected the use of the water-jet in England for the purpose of rapidly cooling the heated plates. The principle adopted in the design of the compound plates has been again utilised by Harvey, who places the soft steel or nickel steel plate in a furnace of suitable construction, and covers it with carbonaceous material such as charcoal, and strongly heats it for a period, which may be as long as 120 hours. This is the old Sheffield process of cementation. The result is to increase the carbon from 0.35 per cent. in the body of the plate to 0.6 per cent. or more at the front surface, such increase only extending to a depth of 2 or 3 inches in the thickest armour.

The carburised face is then "water-hardened," the result being that the best chrome-steel shot are shattered at the moment of impact, unless they are of very large size as compared with the thickness of the plate. The intense hardness of the chilled plates gave rise at first to some little difficulty when it was desired to drill them for the purpose of attaching fittings when in position upon the ship; this has, however, been surmounted by adopting the device of heating the required portion of the plate locally by the aid of electric arcs, and thus to anneal it sufficiently to allow of the subsequent use of ordinary metal working tools.

D. Carnegie<sup>2</sup> has recently stated that modern projectiles are composed of steel containing carbon, associated with one or more of the metals nickel, chromium, manganese, and molybdenum. In hardening, three mediums are used, water, oil, and air. These mediums differ in intensity of action, and the choice of the method to be used is determined by the composition of the material to be hardened. Each medium might also be varied in temperature in the case of water and oil, and in pressure in the case of air. Carbon steels are, as a rule, hardened in water, or partly in water and partly in oil; nickel steels in water, in oil, or in air under pressure; chrome-nickel steels in oil, or in air under pressure; and steels having self-hardening properties, by simply heating and allowing to cool in air.

The penetrating power of projectiles has been increased in recent years by capping,<sup>3</sup> and by improvements in the explosives used.

<sup>1</sup> Weaver, "Notes on Armour," *Journal U.S. Artillery*, vol. iii., 1894, p. 417.

<sup>2</sup> *Min. of Proc. Inst. Civil Eng.*, vol. cliii, pp. 1-57.

<sup>3</sup> *Engineer*, vol. xevii, pp. 21-22.



Another alloy of interest is iron alloyed with 25 per cent. of nickel. Hopkinson has shown that its density is permanently reduced 2 per cent. by an exposure to a temperature of  $-30^{\circ}$ , that is, the metal expands at that temperature. Supposing, therefore, as has been previously stated in this volume, that a ship-of-war was built in our climate of ordinary steel, and clad with some 3000 tons of such nickel-steel armour, we are confronted with the extraordinary fact that if such a ship visited the Arctic regions, it would actually become some 2 feet longer, and the shearing which would result from the expansion of the armour by exposure to cold would destroy the ship.

The immense strides made in recent years in motor-car construction has been largely due to the use of special steels, and Guillet has given an account of these steels used by the French manufacturers.<sup>1</sup>

He divides the steels into the following classes:—

(1) Steels with low percentages of carbon and nickel (Ni 1 to 6 per cent., C 0.1 to 0.25 per cent.), which are used for parts that require case-hardening and quenching—*i.e.* shafts, gears which engage directly, etc.

(2) Steels with medium percentages of carbon and low percentages of nickel (Ni 1 to 6 per cent., C 0.25 to 0.4 per cent.), which are used, after quenching and reheating, for shafts, forgings, axles, bearings, etc.

(3) Steels low in carbon and with high percentages of nickel (Ni 32 to 36 per cent., C 0.12 to 0.2 per cent.), which are used in the making of valves.

(4) Chrome steels with high carbon and low chromium percentages (C 1.0 to 1.2 per cent., Cr 1.0 to 2.5 per cent.), used for bearings.

(5) Silicon steels containing C 0.3 to 0.7 per cent., and Si 0.8 to 2.5 per cent., used for springs.

(6) Chrome-nickel steels (C 0.25 to 0.45 per cent., Ni 2.5 to 2.7 per cent., Cr 0.275 to 0.6 per cent.), employed for numerous parts requiring resistance to shock and a certain degree of hardness.

There is little doubt but that many valuable results will be obtained as a result of the large amount of research work now being carried out in reference to the effect of rare metals on the properties of other metals, and on the correct heat treatment necessary to ensure certain results.

**Colour of Alloys.**—It will now be well to examine some effects of uniting metals by fusing them together, and also to consider the direct influence of a minute quantity of one metal in changing the mass of another in which it is hidden, causing it to behave in a different way in relation to light, and consequently to possess a colour different from that which is natural to it. The

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1905, ii. 166.

added metal may so change the chemical nature of the metallic mass that varied effects of colour may be produced by the action of certain "pickling" solutions. This portion of the subject is so large that reference can only be made to certain prominent facts.<sup>1</sup>

First, with reference to the colour produced by the union of metals. Take, for example, a mass of red copper and one of grey antimony; the union of the two by fusion produces a beautiful violet alloy when the proportions are so arranged that there is 51 per cent. of copper and 49 per cent. of antimony in the mixture. This alloy was well known to the early chemists, but, unfortunately, it is brittle and difficult to work, so that its beautiful colour can hardly be utilised in art. The addition of a small quantity of tin to copper hardens it, and converts it, from a physical and mechanical point of view, into a different metal. The addition of zinc and a certain amount of lead to tin and copper confers upon the metal copper the property of receiving, when exposed to the atmosphere, varying shades of deep velvety brown, characteristic of the bronze which has from remote antiquity been used for artistic purposes. But by far the most interesting copper-alloys, from the point of view of colour, are those produced by its union with zinc, namely, brass. Their preparation demands much care in the selection of the materials.

The most remarkable case known of a coloured alloy is that published by the author,<sup>2</sup> who found that gold alloyed with 10 per cent. of aluminium is brilliantly white, but from this point, as aluminium is added, the tint deepens until flecks of pink appear, and when 78 parts of gold are added to 22 parts of aluminium, an intensely ruby-coloured alloy,  $\text{AuAl}_2$ , is obtained.

The colouring power of metals in alloys is very variable. Ledebur<sup>3</sup> arranges the principal metals in the following order:—Tin, nickel, aluminium, manganese, iron, copper, zinc, lead, platinum, silver, gold.

Each metal in this series has a greater decolorising action than the metals following it. Thus, the colours of the last members are concealed by comparatively small amounts of the first members. A good example is afforded by the alloy used for the Continental nickel coinage. This consists of three parts of red copper with only one part of white nickel. The comparatively small quantity of nickel is, however, sufficient to completely hide the red colour of the copper.

Of the very varied series of alloys the Japanese employ for art

<sup>1</sup> A list of books and papers dealing with the colours of metals and alloys, and with the production of coloured patina, is given by Prof. Ledebur in his work *Die Metallverarbeitung*, 1882, p. 285.

<sup>2</sup> *Proc. Roy. Soc.*, vol. xlix., 1891, p. 347.

<sup>3</sup> *Loc. cit.*, p. 51.

metal-work, the following may be considered the most important and typical. The first is called *shaku-do*; it contains, as will be seen from Analyses Nos. I. and II.,<sup>1</sup> in addition to about 95

	I.	II.
Copper . . . . .	94.50	95.77
Silver . . . . .	1.55	0.08
Gold . . . . .	3.73	4.16
Lead . . . . .	0.11	
Iron and Arsenic . . . . .	traces	
Totals . . . . .	<u>99.89</u>	<u>100.01</u>

per cent. of copper, as much as 4 per cent. of gold. The quantity of gold is, however, very variable, some specimens which have been analysed containing only 1.5 per cent. of the precious metal.

Another important alloy is called *shibu-ichi*. Analyses of this alloy gave:—

	III.	IV.
Copper . . . . .	67.31	51.10
Silver . . . . .	32.07	48.93
Gold . . . . .	traces	0.12
Iron . . . . .	0.52	
	<u>99.90</u>	<u>100.15</u>

There are numerous varieties of it, but in both these alloys, *shaku-do* and *shibu-ichi*, the point of interest is that the precious metals are, as it were, sacrificed in order to produce definite results, gold and silver, when used pure, being employed very sparingly to heighten the general effect. In the case of the *shaku-do*, we shall see presently that the gold appears to enable the metal to receive a beautiful, rich purple coat or patina, as it is called, when treated with certain pickling solutions; while *shibu-ichi* possesses a peculiar silver-grey tint of its own, which, under ordinary atmospheric influences, becomes very beautiful, and to which the Japanese artists are very partial. These are the principal alloys, but there are several varieties of them, as well as combinations of *shaku-do* and *shibu-ichi* in various proportions, as, for instance, in the case of *kiu-shibu-ichi*, the composition of which would correspond to one part of *shaku-do*, rich in gold, and two parts of *shibu-ichi*, rich in silver.

Now, as to the action of pickling solutions.

The Japanese art metal-workers are far ahead of their European brothers in the use of such solutions.

The South Kensington Museum contains a very valuable series

<sup>1</sup> Analyses Nos. I. and III. were made by Prof. Gowland, late of the Imperial Japanese Mint at Osaka; Nos. II. and IV. by Prof. Kalischer, *Dingl. Polyt. Journ.*, vol. cxxv. p. 93.



of fifty-seven oblong plates, some plain and others richly ornamented, which were specially prepared as samples of the various metals and alloys used by the Japanese. The Geological Museum in Jermyn Street has a smaller but more instructive series of twenty-four plates, presented by an eminent metallurgist, the late Mr Hochstätter-Godfrey. From descriptions accompanying the latter, and from information gathered from certain Japanese artificers, it would appear that there are three solutions generally in use. They are made up respectively in the following proportions, and are used boiling:—

	I.	II.	III.
Verdigris . . .	438 grains	87 grains	220 grains
Sulphate of copper .	292 „	437 „	540 „
Nitre . . .	...	87 „	
Common salt . . .	...	146 „	
Sulphur . . .	...	233 „	
Water . . .	1 gallon	...	1 gallon
Vinegar . . .	...	1 gallon	5 fluid drachms

The most widely employed is No. I. When boiled in No. III. solution, pure copper will turn a brownish-red, and *shaku-do*, which contains a little gold, becomes purple. Thus it is possible to appreciate the effect of small quantities of metallic impurity as affecting the colour resulting from the action of the pickle. Copper containing a small quantity of antimony gives a shade very different from that resulting from the pickling of pure copper. But the copper produced in Japan is often the result of smelting complex ores, and the methods of purification are not so perfectly understood as in the West. The result is that the so-called “antimony” of the Japanese art metal-workers, which is present in the variety of copper called *kuromi*, is really a complex mixture containing tin, cobalt, and many other metals, so that a metal-worker has an infinite series of materials at command with which to secure any particular shade; and these are used with much judgment, although the scientific reasons for the adoption of any particular sample may be hidden from him. It is strictly accurate to say that each particular shade of colour is the result of minute quantities of metallic impurity.

There is one other material to the production of which art workmen in this country will, it is to be hoped, soon direct their attention, as the possibilities of its applications are endless. It is called in Japanese *mokumé*, which signifies “wood grain.” It is now very rare, even in Japan, but formerly the best specimens appear to have been made in Nagoya by retainers of the Daimio of Owari.

This diagram (fig. 43) shows the method of manufacture. Take thin sheets of gold, silver, *shibu-ichi*, *shaku-do*, and *kuromi* and



solder<sup>1</sup> them together, layer upon layer, care being taken that the metals which will present diversity of colour come together. Then drill conical holes of varying depth (A) in the mass, or devices in trench-like cuts of V section (B), and then hammer the mass until the holes disappear; the holes will thus be replaced by banded circles and the trenches by banded lines. Similar effects may be produced by taking the soldered layers of the alloy, and, by the aid of blunted tools, making depressions on the back of the mass, so as to produce prominences on the front (C). These prominences are filed down until the sheet is again flat; the banded alloys will then appear on the surface in complicated sections, and a very remarkable effect is produced, especially when the colours of the alloys are developed by suitable "pickles." In this way any device may be produced. In principle the method is the same as that which produces the damascening of a sword-blade or gun-barrel, and depends on the fact that, under certain conditions, metals behave like viscous

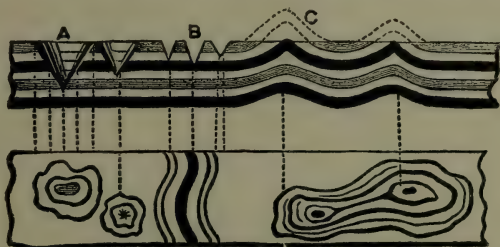


FIG. 43.

solids, and as truly "flow" as pitch or honey does. In the case of *mokumé* the art-workman has a wide range of tinted metals at command.

The Oriental art metal-workers often blend metals and alloys of different colours by pouring them together at a temperature near the solidifying point of the more infusible of the metals and alloys to be associated. In this way, by pouring the comparatively fusible grey silver-copper alloy on to fused copper which is just at the point of "setting," the metals unite, but do not thoroughly mix, and a mottled alloy is produced. The Japanese use such alloys in almost every good piece of metal-work.

**Alloys of Industrial Importance.**—The following tables indicate the composition of some of the more important alloys, which have been selected in order to give the student an idea of the way in which for industrial use metals are associated. The list is, however, necessarily a limited one, and reference should be made for fuller information to the standard treatises, of which

<sup>1</sup> The following solder was found to answer well:—Silver, 55.5; zinc, 26.0; copper, 18.5.

a list is appended:—R. H. Thurston, Report on a Preliminary Investigation of the Properties of the Copper-Tin Alloys, Washington, 1879; A. Guettier, *Guide Pratique des Alliages Métalliques*, Paris, 1865; Roberts-Austen, The Alloys used for Coinage (Cantor Lectures, Society of Arts), 1884; A. Ledebur, *Metallverarbeitung*, Brunswick, 1882; Brannt, Krupp, and Wildberger, "The Metallic Alloys," Philadelphia, 1889; Reports of Alloys Research Committee, *Proc. Inst. Mech. Engineers*, 1891, 1893, 1895, 1897, 1899, 1904, 1905, and 1907; *Brasses, Bronzes, and other Alloys*, Thurston, New York, 1893; *Iron, Steel, and other Alloys*, H. M. Howe, 1903; *Étude Industrielle des Alliages Métalliques*, L. Guillet, Paris, 1906; *Alloys*, Law, 1908.

## COPPER-ZINC ALLOYS.

	Cu.	Zn.		Cu.	Zn.
Tombac for buttons . . . . .	99·15	0·85	Bristol metal . . . . .	75·00	25·00
Red Tombac, Vienna . . . . .	97·80	2·20	Sheet brass . . . . .	74·58	25·42
Pinchbeck . . . . .	93·60	6·40	Chrysorin . . . . .	72·00	28·00
Red Tombac, Paris . . . . .	92·00	8·00	Common brass . . . . .	66·60	33·40
French gold . . . . .	90·00	10·00	Forging brass . . . . .	66·00	34·00
Brass for very delicate castings . . . . .	86·00	14·00	Good wire brass . . . . .	65·40	34·60
Paris jewelry . . . . .	85·00	15·00	Mosaic gold . . . . .	65·30	34·70
Gold leaf . . . . .	84·21	15·79	Muntz metal . . . . .	60·00	40·00
Bronze powder . . . . .	83·02	16·98	Very ductile brass . . . . .	54·00	46·00
Bath metal . . . . .	82·95	17·05	German brass . . . . .	49·47	50·53
Red-yellow jewelry . . . . .	82·50	17·50	Strong solder for brass . . . . .	33·34	66·66
Dutch brass . . . . .	79·56	20·44	Watchmakers' brass . . . . .	32·85	67·15
Vienna gold leaf . . . . .	77·50	22·50	White button metal . . . . .	19·65	80·35

## COPPER-TIN ALLOYS.

	Cu.	Sn.
Mild bronze . . . . .	92·00	8·00
Ordnance metal . . . . .	91·70 to 88·39	8·30 to 11·61
Toothed wheels . . . . .	91·30	8·70
Railway car bearings . . . . .	90·00	10·00
Carriage wheel boxes . . . . .	84·00	16·00
Chinese gong . . . . .	80·43	19·57
Bell metal . . . . .	77·50	22·50
„ (Big Ben) . . . . .	75·80	24·20
Swiss clock bells . . . . .	75·00	25·00
Speculum metal . . . . .	68·21	31·79
„ . . . . .	66·60	33·40
White bell metal . . . . .	40·00	60·00

## COPPER-NICKEL ALLOYS.

	Cu.	Ni.	Zn.
Nickel coin . . . . .	75.0	25.0	
German silver . . . . .	55.0	17.5	28.5
English "German silver" . .	62.4	15.05	22.15
Vienna    "    " . . . . .	50.0	25.0	25.0
"    "    " . . . . .	60.0	20.0	20.0
Chinese    "    " . . . . .	26.3	36.8	36.8
Paris white metal . . . . .	69.8	19.8	5.5
Packfong (Chinese alloy) . .	43.8	15.6	40.6
Berlin Argentan . . . . .	56.0	26.0	22.0

## OTHER COPPER ALLOYS.

	Cu.	Zn.	Sn.	Other Constituents.
Metal for cocks . . . . .	88.0	2.0	10.0	
Bearing metal for loco axles .	82.0	8.0	10.0	
"    hard . . . . .	82.0	2.0	16.0	
"    medium hard . . . .	69.5	5.8	21.7	
"    for railroad car axles	75.0	2.0	20.0	
Metal for steam whistles . .	80.0	2.0	18.0	
"    mechanical instruments	81.2	5.1	12.8	
Algier's metal . . . . .	5.0	...	94.5	Sb 0.5
Sterro    " . . . . .	55.33	41.8	...	Fe 4.66
Aich's    " . . . . .	60.0	38.12	...	Fe 1.5
Japanese art bronze . . . . .	82.7	1.8	4.7	Pb 9.9
"    " . . . . .	71.4	6.0	5.9	Pb 16.3
Chinese    " . . . . .	74.0	10.0	1.0	Pb 15.0
Egyptian chisel . . . . .	94.0	...	5.9	Fe 0.1
Attic coin . . . . .	88.46	...	10.04	Pb 1.5
Manganese bronze . . . . .	83.45	...	...	Mn 13.48 ; Fe 1.24
"    " . . . . .	81.03	...	...	Mn 16.86 ; Fe 1.67

## TIN ALLOYS.

	Sn.	Sb.	Cu.	Other Constituents.	Remarks.
Britannia metal	90·62	7·81	1·46	...	Birmingham sheet. For bearings. The composition of white metal is very variable.
White metal	82·00	12·00	6·00	...	
„	53·00	10·60	2·40	Pb 33·0 ; Zn 1·0	
Ashberry metal	77·8	19·4	...	Zn 2·8	The melting-point increases with the proportion of lead.
Pewter	80·0	...	...	Pb 20·0	
Solder, fine	66·6	...	...	Pb 33·3	
„ tin	50·0	...	...	Pb 50·0	Authorised by the Plumbers' Com- pany.
„ plumbers'	33·3	...	...	Pb 66·6	

## LEAD ALLOYS.

	Pb.	Sb.	Sn.	Other Constituents.	Remarks.
Type metal	70·0	18·0	10·0	Cu 2·0	For stereotyping. For slowly revol- ving axles.
„	82·0	14·8	3·2	...	
Bearing metal	84·0	16·0	...	...	
„	60·0	20·0	20·0	As 0·2 to 0·35	
Shot metal	99·6	...	...		

## ZINC ALLOYS.

	Zn.	Sn.	Cu.	Other Constituents.	Remarks.
Antifriction metal	85·0	...	5·0	Sb 10·0	For bearings. (Ledebur).
Babbitt's metal	69·0	19·0	4·0	Sb 3·0 ; Pb 5·0	



## BISMUTH ALLOYS (FUSIBLE METAL).

	Bi.	Pb.	Sn.	Cd.	Melting-point.
					° C.
Newton's alloy . .	50·0	31·25	18·75	...	95
Rose's „ . .	50·0	28·10	24·64	...	100
Darcet's „ . .	50·0	25·00	25·00	...	93
Wood's „ . .	50·0	24·00	14·00	12·00	66-71
Lipowitz's „ . .	50·0	27·00	13·00	10·00	60

## ALLOYS FOR COINAGE.

	Au.	Cu.	Ag.	Other Constituents.	Remarks.
Gold coin . .	91·66	8·33	...	...	British standard.
„ . .	90·0	10·0	...	...	“Latin Union” and American.
„ . .	1·33	82·73	15·93	...	Roman, Septimus Severus, 265 A.D.
Silver coin . .	0·1	7·1	92·5	Pb 0·2	Roman, B.C. 31, almost same as British silver coin.
Gold coin . .	40·35	19·63	40·02	...	Early British, B.C. 50.
Silver coin . .	...	7·5	92·5	...	British standard.

## CHAPTER IV.

### THE THERMAL TREATMENT OF METALS.

**Annealing, Hardening, and Tempering.**—The mechanical properties of metals are often, in a great measure, dependent on the thermal treatment to which they have been subjected. There can be no question that the application of heat to a metal may produce a remarkable molecular change in its structure, the nature of the change depending on that of the metal or alloy, and on the treatment it has undergone. It will be well, therefore, to consider carefully what happens when metals are submitted to the three principal operations involving thermal treatment, which are known respectively as **annealing, hardening, and tempering**. Usually all three are intimately related. Annealing may be defined as the release of strain in metals, which may itself have been produced by mechanical treatment, such as hammering, rolling, or wiredrawing, or by either rapid or slow cooling from a more or less elevated temperature. As an example of the former, it may be mentioned that metals and alloys which have been rendered excessively hard by rolling are heated usually to bright redness and allowed to cool slowly. In the case of copper, it does not appear to be important whether the cooling is slow or rapid, and in recent years much experimental evidence has been accumulated which tends to show that in the case of certain metals which have been hardened, a more or less prolonged exposure to a temperature under  $100^{\circ}$  will sensibly anneal them. With some metals and alloys, the rapidity with which the cooling is effected is very important. Bronze containing about 20 per cent. of tin<sup>1</sup> is rendered very malleable by rapid cooling. It is, however, in the case of iron and steel that thermal treatment is especially important, although many other alloys may undergo important changes in properties by varying the thermal treatment.

Steel, it must be remembered, is modified iron. The name "iron" is, in fact, a comprehensive one, for the mechanical behaviour of the metal is so singularly changed by influences acting from within

<sup>1</sup> Riche, *Ann. de Chim. et de Phys.*, vol. xxx. (1873), p. 417.

and without its mass as to lead many to think, with Paracelsus, that iron and steel must be two distinct metals, their properties being so different. Pure iron may be prepared in a form pliable and soft as copper, steel can readily be made sufficiently hard to scratch glass; and notwithstanding this extraordinary variance in the physical properties of iron and certain kinds of steel, the chemical difference between them is comparatively very small, and would hardly secure attention if it were not for the importance of the results to which it gives rise. It is necessary to consider the nature of the transformations which iron can sustain, and to see how it differs from steel, of which an old writer has said:<sup>1</sup> "Its most useful and advantageous property is that of becoming extremely hard when ignited and plunged in cold water, the hardness produced being greater in proportion as the steel is hotter and the water colder. The colours which appear on the surface of steel slowly heated direct the artist in *tempering* or reducing the hardness of steel to any determinate standard." There is still so much confusion between the words "temper," "tempering," and "hardening," in the writings of even very eminent authorities, that it is well to keep these old definitions carefully in mind. **Hardening** is the result of rapidly cooling a strongly heated mass of steel. **Tempering** consists in modifying or reducing the hardness by heating the hardened steel to a temperature far short of that to which it was raised before hardening; this heating may or may not be followed by rapid cooling. **Annealing**, as applied to steel, consists in heating the mass to a temperature higher than that used for tempering, and allowing it to cool slowly.

The effects of the above treatments may be illustrated by taking a strip of steel and cutting it into three pieces. One piece can be bent cold, showing that it is soft; but if it is heated to redness and plunged in cold water it will become hard, and will break on any attempt to bend it. The second piece may, after heating and rapid cooling, be again heated to about the melting-point of lead, when it will bend readily, but will spring back to a straight line when the bending force is removed. The third piece may be softened by being cooled slowly from a bright red heat, and this will bend easily and will remain distorted.

The metal has been singularly altered in its properties by comparatively simple treatment, and all these changes, it must be remembered, have been produced in a solid metal to which nothing has been added, and from which nothing material has been taken away.

The theory of the operation described above has been laboriously built up, and its consideration introduces many questions of great interest, both in the history of science and in our knowledge of molecular physics.

<sup>1</sup> *The First Principles of Chemistry*, by W. Nicholson, London, 1760, p. 312.

**History.**—First, as regards the history of the subject. The knowledge that steel might be hardened must have been derived from remote antiquity. Copper hardened with tin was its only predecessor, and it continued to be used very long after it was known that steel might be hardened. It would, moreover, appear that a desire to appreciate the difficulties of a people to whom cutting instruments of hard steel were unknown, seems to have induced experimenters in quite recent times to fashion implements of bronze, and a trustworthy authority states that “Sir Francis Chantry formed an alloy containing about 16 parts of copper,  $2\frac{1}{2}$  of zinc, and  $2\frac{1}{2}$  of tin, of which he had a razor made, and even shaved with it.”<sup>1</sup> The Greek alchemical MSS., which have been so carefully examined by M. Berthelot, give various receipts, from which it is evident that in the early days the nature of the quenching fluid was considered to be all-important. There were certain rivers the waters of which were supposed to be specially efficacious. Pliny, who says that the difference between waters of various rivers can be recognised by workers in steel, also knew that oil might be used with advantage for hardening certain varieties of the metal. It is sad to think how many of the old recipes for hardening and tempering have been lost. Theophilus, writing in the eleventh century, gives very quaint instructions in the art of hardening steel. The belief, however, in the efficacy of curious nostrums and solutions for hardening steel could hardly have been firmer in the third century B.C. than in the sixteenth of our era. Pure cold water is now usually employed for hardening, but it was far too simple a material for many a sixteenth-century artificer to employ, as is shown by the quaint recipes contained in one of the earliest books of trade secrets, which, by its title, showed the existence of the belief that the “right use of alchemy” was to bring chemical knowledge to bear upon industry. The earliest edition was published in 1531,<sup>2</sup> and the first English translation<sup>3</sup> in 1583, from which the following extracts may be of interest. “Take snayles, and first drawn water of a red die, of which water being taken in the two first monthes of harvest when it raynes,” boil it with the snails, “then heate your iron red hot and quench it therein, and it shall be hard as steele.” “Ye may do the like with the blood of a man of xxx years of age and of a sanguine complexion, being of a merry nature and pleasant . . . distilled in the middst of May.” This may seem trivial enough, but the belief in the efficacy of such solutions survived into the nineteenth century, for in a work published in 1810 the artist is

<sup>1</sup> *Engines of War*, by H. Wilkinson, 1841, p. 194.

<sup>2</sup> *Rechter Gebrauch d. Alchimei*, 1531. There were many English editions.

<sup>3</sup> “A profitable boke declaring dyuers approued remedies,” etc., London, 1583. See Prof. Ferguson’s learned paper “On some Early Treatises on Technological Chemistry,” *Phil. Soc. Glasgow*, Jan. 1886, vol. xvii. p. 206.



prettily directed<sup>1</sup> "to take the root of blue lilies, infuse it in wine and quench the steel in it," and the steel will be hard; on the other hand, he is told that if he "takes the juice or water of common beans and quenches iron or steel in it, it will be soft as lead." As must always be the case when the practice of an art is purely empirical, such procedure was often fantastic, but it is by no means obsolete, for probably at the present day there are many workshops in which some artificer could be found with a claim to possess a quaint nostrum for hardening steel. Even the use of absurdly compounded baths was supported by theoretical views. Otto Tachen,<sup>2</sup> for instance, writing of steel in about the year 1666, says that steel when it is "quenched in water acquires strength, because the light alcaly in the water is a true comforter of the light acid in the iron, and cutlers do strengthen it with the alcaly of animals," hence the use of snails. Again, Lemery<sup>3</sup> explains in much the same way the production of steel by heating iron in the presence of horns of animals.

These points have been dwelt upon in order to bring out clearly the fact that the early workers attached great importance to the nature of the fluid in which hot steel was quenched, and they were right, though their theories may have been wrong. The degree of rapidity with which heat is abstracted from the steel during the operation of hardening is as important at the present day as it ever was. Roughly speaking, if steel has to be made glass-hard, ice-cold water, brine, or mercury is used; if it has only to be made slightly hard, hot water or oil may be employed; while, as Thomas Gill<sup>4</sup> suggested in 1818, both "hardening" and "tempering" may be united in a single operation by plunging the hot metal in a bath of molten lead or other suitable metal, which will, of course, abstract the heat more slowly.

The use of lead and of other metals in hardening steel has, however, long been known. Réaumur<sup>5</sup> described in 1722 a method of hardening the points of tools by forcing them when hot into *solid* tin and lead, and he hints at the use of solid masses of gold, silver, and copper as cooling metals. This old work blends curiously into the new, for the cold metallic surfaces suggested by Clémendot<sup>6</sup> doubtless play an important part in his process of hardening by compression; whilst another process, that of hardening by water spray, which is used in connection with the manufacture of armour-plate, is at least a century old.<sup>7</sup>

Probably the earliest reference to the use of mercury as a

<sup>1</sup> *The Laboratory; or School of Arts*, 6th edition, 1739, p. 126. There is a later edition of 1810.

<sup>2</sup> *Key to the Ancient Hippocratical Learning*, London, 1690, p. 68.

<sup>3</sup> *A Course of Chymistry*, 2nd edition, 1686, p. 131.

<sup>4</sup> Thomson's *Annals of Philosophy*, vol. xii. (1818), p. 58.

<sup>5</sup> *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 351.

<sup>6</sup> *Comptes Rendus*, vol. xciv. (1882), p. 703.

<sup>7</sup> Guyton de Morveau, *Encyc. Méthodique*, Paris, 1786, p. 436.

cooling fluid is that made by Réaumur; but in no direction has the modern development of hardening processes been more important than in connection with the use of baths, in which the fluid, being a molten metal, is not readily vaporised. Lisbonne<sup>1</sup> has shown what remarkable results as regards resistance to penetration have attended the adoption of the process of hardening armour-plates in lead baths, which, as Éverard<sup>2</sup> shows, must be capacious and not heated above the melting-point of lead, his experiments leading to the conclusion that armour-plates so quenched in lead are very difficult to penetrate, and present great resistance to fracture.

**Internal Constitution of Steel.**—The development of theories relating to the internal constitution of steel must now be traced. The advent of the Phlogistic school with the teaching of Becher and Stahl led to the view that iron gained phlogiston during its conversion into steel. By phlogiston the early chemists really meant *energy*, but to them phlogiston was represented to be a kind of soul possessed by all metals, which they could lose by burning and regain by the process they called “revivication.” “Hardness [in metals] is caused by the jeunenesse of the spirit and their imparity with the tangible parts,” said Francis Bacon;<sup>3</sup> while, according to Stahl,<sup>4</sup> steel was merely iron possessing, in virtue of its phlogiston, the characteristics of a metal in a higher degree, and this view prevails in the writings of Henckel, Newmann, Cramer, Gellert, Rinman, and Macquer. This opinion survived with wonderful persistence, but it did not influence the teaching of Réaumur,<sup>5</sup> who, in 1722, was the first to suggest a physical theory which has been in any way justified by modern research. He assumed that when steel was heated, “sulphurs and salts” were driven out from the molecules, which he represents diagrammatically, into the interstitial space between them. The quenching of the steel and its sudden cooling prevented the sulphurs and salts from returning into the molecules, which were thus firmly cemented by the matter between them, and hard, rigid steel was the result. In tempering, the sulphurs and salts partially returned into the molecules, and the metal became proportionately soft. He used the Torricellian vacuum to demonstrate that the hardening of steel is not accompanied by the evolution of gas; and he concluded that “since the hardening of steel is neither due to the intervention of a new substance nor to the expulsion of air, it only remains to seek its cause in the changes occurring in its structure.” Notwithstanding this, the

<sup>1</sup> *Génie civil*, vol. xiii. (1888), p. 22.

<sup>2</sup> Paper read at the International Congress of Mining and Metallurgy, Paris, 1889.

<sup>3</sup> *Sylva Sylvarum*, 2nd edition, 1628, p. 215.

<sup>4</sup> *Fundamenta Chemicæ*, part iii. p. 451, quoted by Guyton de Morveau in the article “Acier,” *Encyc. Méthodique*, p. 421, Paris, 1786.

<sup>5</sup> *L'art de convertir le fer forgé en acier*, Paris, 1722, p. 321 et seq.

Phlogistic school were not daunted; and this leads directly to the work of Torbern Bergman, the great Professor at the University of Upsala, who, in 1781, showed<sup>1</sup> that steel mainly differs from iron by containing about  $\frac{2}{10}$  per cent. of plumbago, while iron does not. Read in connection with modern research, his work seems wonderfully advanced. He was so forcibly impressed by the fact that the great difference in the mechanical properties of different specimens of iron is due to the presence of small quantities of impurity, and that the properties of iron do not vary, as he says, unless by chance the iron has gathered foreign matter, "*nisi forte peregrinum paullo uberius inhæreat metallum,*" in which sentence there is even the dawn of the view that, under the influence of small quantities of foreign matter, iron is, as he calls it, polymorphous, and plays the part of many metals. "*Adeo ut jure dici queat, polymorphum ferrum plurimum simul metallorum vices sustinere.*"<sup>2</sup> Unfortunately he confounded the plumbago or carbon he had isolated with phlogiston, as did Rinman in 1782, which was strange, because in 1774 the latter physicist had shown that a drop of nitric acid simply whitens wrought iron, but leaves a black stain on steel. Bergman tenaciously held to the phlogistic theory in relation to steel; it was inevitable that he should. The true nature of oxidation had been explained; no wonder that the defenders of the phlogistic theory should seek to support their case by appealing to the subtle and obscure changes produced in iron by such apparently slight causes. Bergman's view was, however, combated by Vandermonde, Berthollet, and Monge,<sup>3</sup> who showed in a report communicated to the *Académie des Sciences* in 1786 that the differences between the main varieties of iron is determined by variation in the amount of carbon; and further, that steel must contain a certain quantity of carbon in order that it might possess definite qualities. Bergman died in 1784, and the report to which reference has been made is full of respect for "this grand chemist," as its authors call him, "whom science had lost too soon."

Kirwan's essay on Phlogiston,<sup>4</sup> in which Bergman's views were defended, elicited a reply from Lavoisier himself, and brought down the French school in strength to contest almost the last position occupied by the believers in phlogiston.<sup>5</sup>

Bergman's was almost the first calorimetric work, and it is impossible to read it without feeling that in paying the just tribute to Lavoisier's genius, Bergman has been overlooked. He desired

<sup>1</sup> *Opuscula Physica et Chemica*, vol. iii., Upsala, 1783; *De Analyti Ferri*, a dissertation delivered June 9, 1781.

<sup>2</sup> *De Analyti Ferri*, p. 4.

<sup>3</sup> *Histoire de l'Académie Royale des Sciences*, 1786 (printed 1788), p. 132.

<sup>4</sup> *Essay on Phlogiston and the Constitution of Acids*, 1787, p. 134.

<sup>5</sup> *Essai sur le Phlogistique traduit de l'Anglais de M. Kirwan, avec des Notes de MM. de Morveau, Lavoisier, de la Place, Monge, Berthollet, et de Fourcroy*, Paris, 1788.



to ascertain whether pure iron, steel, and cast iron contain the same amount of heat. He therefore attacks the materials with a solvent, and notes the heat evolved. He says the solvent breaks up the assemblage of the aggregation of molecules and forms other unions. If the new body demands more heat than the body which has been disunited, then the thermometer falls. If, on the other hand, the degree of heat required is less, the environment will be heated, which will result in the rise of the thermometer. In modern language, when a chemical compound is formed, heat is evolved and energy is lost, but if one substance, say a metal, simply dissolves another, the solution is attended with absorption of heat, and the product, when attacked by a suitable solvent, should evolve practically the same amount of heat, but certainly not less than would be evolved by the individual metals present in solution.<sup>1</sup> This is specially interesting from its relation to the calorimetric work of Lavoisier and Laplace in 1780, and of Lavoisier



FIG. 44.

in 1782, which led him to explain the nature of oxidation, and to show that a metal could be as truly calcined or oxidised by the action of a solution as by the action of air at an elevated temperature. Now that the importance of thermal chemistry is beginning to be recognised in relation to industrial chemistry and metallurgy, it is to be hoped that Bergman's merits will be more fully considered. The main point is, that he taught that the difference between iron and steel consists in the  $\frac{2}{10}$  to  $1\frac{1}{2}$  per cent. of carbon which steel contains.

It was only natural that Black, writing in 1796, should have attributed the hardening of steel to the "extrication of latent heat," "the abatement of the hardness by the temper" being due, he says, "to the restoration of a part of that heat";<sup>2</sup> still he recognised that the work of Bergman had entirely changed the situation. The next step was made in France. It was considered necessary to establish the fact that carbon is really the element which gives steel its characteristic properties, and with this object in view Clouet,<sup>3</sup> in 1798, melted a little crucible of iron, weighing 57·8 grammes, containing a diamond, weighing 0·907 gramme, and obtained a fused mass of steel. Fig. 44 shows a plan of the iron crucible and diamond from the drawing in Guyton de Morveau's paper.

His experiment was repeated by many observers, but the results were open to doubt from the fact that furnace gases could always obtain access to the iron, and might, as well as the diamond,

<sup>1</sup> See French translation of Bergman's work, Paris, 1783, p. 72.

<sup>2</sup> *Lectures on the Elements of Chemistry*, vol. ii. (1803), p. 505.

<sup>3</sup> Experiment described by Guyton de Morveau, *Ann. de Chim.*, vol. xxxi. (1799), p. 328.



have yielded carbon to the iron. The carbon might have been presented to the iron in the form of a gas capable of yielding carbon, and this element would as surely have found its way into the steel.

Margueritte,<sup>1</sup> for instance, in 1865, repeated Clouet's experiment, and showed that although carburisation can be effected by simple contact of iron and carbon, it is nevertheless true that in the ordinary process of cementation the gas carbonic oxide plays an important part, which had until then been overlooked. The discovery of Graham,<sup>2</sup> in 1866, of the occlusion of carbonic oxide by iron, gave additional support to this theory.

The question, however, of the direct carburisation of iron by the diamond has never been doubted since 1815, when a working cutler, W. H. Pepys,<sup>3</sup> heated iron wire and diamond dust together and obtained steel, the heat being afforded by a powerful electric battery. The absorption of carbon in the diamond form by iron may be made clear by reference to the diagram (fig. 45), which represents a glass vessel, which may either be rendered vacuum or may be filled with an atmosphere of gas through the tube *d*. An iron wire *b*, placed between the terminals of a battery *cc'*, is heated to redness, and remains glowing until it is touched by pure diamond dust, which is effected by raising the cup *a*. The iron combines with the diamond dust and fuses.

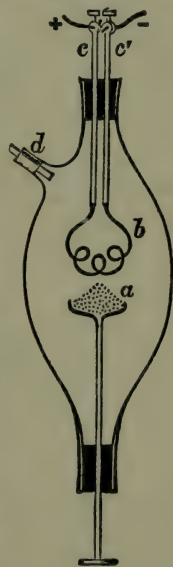


FIG. 45.

It must not be thought, however, that the steel owes its hardness to the passage of diamond into the iron as *diamond*. Margueritte's form of Clouet's experiment may be repeated by using a vacuum instead of an atmosphere of gas, and employing the form of apparatus shown in fig. 46, which represents an arrangement for heating the diamond and iron *in vacuo*. A strip of pure iron *b* is placed between two terminals *cc'*, which are connected with an electric supply. The vessel (of glass) is rendered vacuum by connecting the tube *d* with a Sprengel pump. The iron is then heated by an electric current and maintained glowing until all occluded gas is expelled from the iron, which is then allowed to cool *in vacuo*. Small, pure diamonds *a a' a''* are then placed on the strip of iron through the orifice into which the tube *d* fits. The vessel is rendered vacuum, and when the iron is again heated in contact with the diamonds it fuses and combines with them.

<sup>1</sup> "Sur l'aciation," *Ann. Chim. et Phys.*, t. vi., 1865, p. 55.

<sup>2</sup> *Phil. Trans. Roy. Soc.*, 1866, pp. 399-439.

<sup>3</sup> *Ibid.*, 1815, p. 371.

The diamond by union with iron has passed, partially at least, to the other form of carbon, graphite; while treatment with a solvent which removes the iron shows that carbon has entered into intimate association with the iron, a fact which leads us to the next step in the study of the relations between carbon and iron.

Hempel<sup>1</sup> has shown that, in an atmosphere of nitrogen, solid iron appears to assimilate the diamond form of carbon more readily than either the graphitic or the amorphous forms, but directly carbon is associated with *molten* iron it behaves like the protean element it is, and the state which this carbon assumes is influenced by the rate of cooling of the molten mass, or even by the thermal treatment to which the solidified mass is subjected. As carbon is well known to exist in the distinctive forms of diamond, graphite, and soot, it need not be considered strange that carbon should be capable of being present in intimate association with iron, but in very varied forms.

The mode of existence of carbon in soft annealed steel is very different from that in which it occurs in hard steel. Karsten

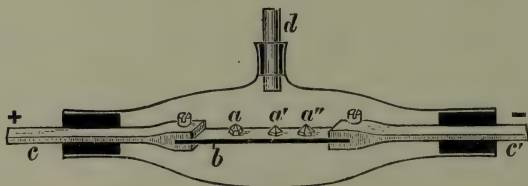


FIG. 46.

was the first to isolate, in 1827, from soft steel, a true compound of iron and carbon; Berthier<sup>2</sup> also separated from soft steel a carbide of iron, to which he assigned the formula  $\text{FeC}$ ; and it need only be added that Sir F. Abel<sup>3</sup> gave much experimental evidence in favour of the existence in cold-rolled steel of a carbide,  $\text{Fe}_3\text{C}$ , which he isolated by the slow solvent action of a chromic acid solution. His work has been accepted as conclusive, and has been the starting-point of much that has followed.

Obviously the microscope should reveal wide differences between the structure of various kinds of iron and steel; and the late Dr Sorby, in his very delicate investigations into the structure of steel,<sup>4</sup> has shown that this is the case, the point of main importance being the existence of a substance which Sorby called the "pearly constituent" in soft steel. This pearly constituent is closely related to the carbide of iron,  $\text{Fe}_3\text{C}$ , of Abel, and is a mechanical mixture of  $\text{Fe}_3\text{C}$  and pure iron. Its presence

<sup>1</sup> *Ber. der. deutsch. chem. Gesellschaft*, vol. xviii. (1885), p. 998.

<sup>2</sup> *Ann. des Mines*, vol. iii. (1833), p. 229.

<sup>3</sup> *Proc. Inst. Mech. Eng.* (1883), p. 56.

<sup>4</sup> *Journ. Iron and Steel Inst.*, No. 1 (1887), p. 255.

is diagrammatically indicated in fig. 47. The diagram will serve for the purpose of illustration to indicate the appearance when soft, hardened, and tempered steel are respectively treated with a solvent which acts gently on the mass.

The late M. Osmond prepared the following micro-sections of different varieties of steel expressly for this volume. The degree of carburisation varies from 0.45 to 1.60 per cent. of carbon, and the thermal treatment of the steel was in all cases different.

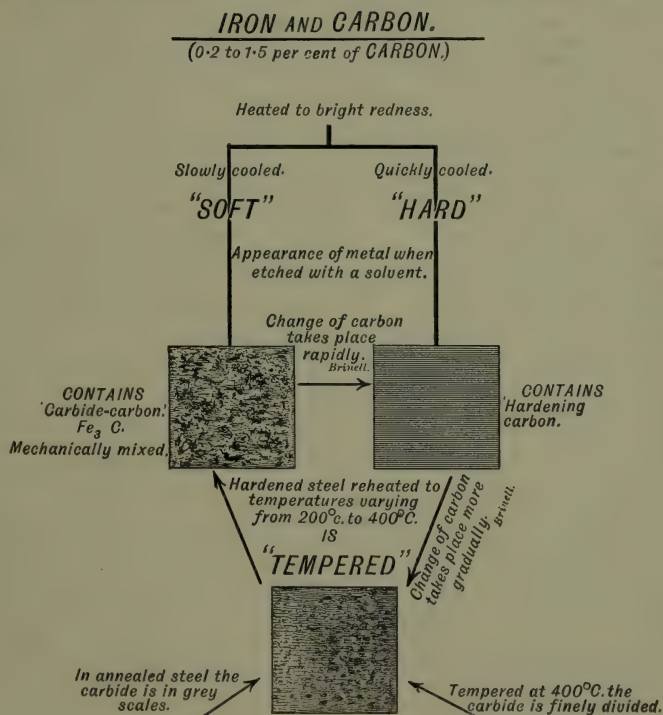


FIG. 47.

The method of preparing such micro-photographs is described on p. 213, and it must be remembered that the preparation and interpretation of such sections demands much experience. It is necessary to state at the outset that, in accordance with a suggestion made by Howe, mineralogical names have been given to the various constituents of steel, in order to facilitate their identification. For micrographic purposes steel is viewed as if it were a rock with various minerals distributed through it. Thus iron free from carbon is called *Ferrite*, and is left white and brilliant



when the polished specimen is treated with a solution of iodine or picric acid. Strong nitric acid also does not stain it, but the use of this reagent is not to be recommended to beginners in micro-graphic investigation.

*Cementite*, another constituent of steel, is a carbide which corresponds to the formula  $\text{Fe}_3\text{C}$ . It remains bright after the polished section of steel is attacked by iodine solution. It is hard, and stands in relief when the steel is polished with the finest rouge on parchment placed on a soft support such as wood.

*Pearlite* is an intimate mixture of ferrite and cementite; it is a very characteristic constituent of steel which has been slowly cooled from a high temperature, and if the steel contains 0.9 per cent. of carbon the mass will consist wholly of pearlite. It may be coloured dark by iodine solution, and its presence is best revealed when the steel is polished in relief by the method which has just been indicated, or treated with a 5 per cent. solution of picric acid in alcohol. Pearlite may exist in several conditions in steel, according to the rate at which the metal has cooled down; granular pearlite is obtained after fairly rapid cooling, laminated pearlite after very slow cooling, in which case the striæ are alternately hard and soft, and segregated pearlite after extremely slow cooling, in which case the parallel striæ disappear and the  $\text{Fe}_3\text{C}$  forms irregular massive segregations.

*Martensite* is the very hard micro-constituent of which hardened steel consists. It appears like a system of interlacing crystalline fibres. This structure is well developed by the *polish attack*. According to Sauveur, this consists of a solution of carbon in  $\beta$  iron.

*Troostite*,<sup>1</sup> according to Osmond, is an intermediate structure which occurs on the transformation of martensite into pearlite, and *vice versâ*. This is obtained on quenching specimens during the critical range of temperature; it is easily recognised on etching with HCl in alcohol (1 to 100), as it colours dark, while martensite remains unaffected. According to Sauveur, this consists of a solution of carbon in  $\alpha$  iron.

*Sorbite*,<sup>1</sup> according to Osmond, is a transition structure which occurs between troostite and pearlite, but is now generally considered to be granular or sorbitic pearlite (emulsified pearlite of Arnold). It is obtained by cooling small samples in the air, or by quenching in molten lead.

*Austenite* is a constituent first identified by Osmond in high carbon steel which had been quenched from a high temperature in iced brine;<sup>2</sup> this has no well-defined structure, and is considered by Sauveur to be a solution of carbon in  $\gamma$  iron.

As M. Osmond pointed out, the two reagents, a solution of iodine or an infusion of liquorice, enable the micro-structures of steel to be divided into two groups, in both of which, however,

<sup>1</sup> See special note on page 161.

<sup>2</sup> *Comptes Rendus*, vol. cxxi., 1895, p. 684.



martensite finds a place. These groups are (a) not coloured by infusion of liquorice—ferrite, cementite, and martensite; (b) coloured by liquorice—martensite, troostite, or sorbite. Martensite, which only assumes a yellowish tinge, may be recognised by its crystalline form. A dilute solution of iodine will, moreover, by acting on a polished surface, enable the structures to be again divided. Those which are not coloured by iodine are ferrite or cementite, while those which are coloured are sorbite, troostite, or martensite. These reagents, however, have been more or less superseded by such solutions as nitric or picric acids in alcohol; with the latter, the ferrite is not attacked or coloured, and the mottled appearance often caused by nitric acid is avoided. Le Chatelier uses a boiling alkaline solution of picric acid containing 25 per cent. NaOH and 2 per cent. picric acid to distinguish cementite from other constituents, this being the only one to be coloured by the solution.

In order to distinguish troostitic and sorbitic structures from others, a freshly prepared solution of the following composition is used: 1 part of a 4 per cent. nitric acid solution in acetic anhydride is added to 3 parts of a solution made up of equal parts of methyl, ethyl, and iso-amyl alcohols. This solution colours only troostite and sorbite in ten minutes.

All the micro-sections of which the following photographs are given were magnified 1000 diameters. With the exception of fig. 52, they were all prepared by polishing and treatment with the infusion of liquorice. Fig. 52 was simply polished in relief on a soft base.

Figs. 48, 49, 50, 51 represent steel which contains 0.45 per cent. of carbon. Fig. 48 represents this variety of steel which has been forged and annealed at a temperature of 750°. It shows ferrite and pearlite, certain portions of the pearlite passing into sorbite. There are also a few grains of entangled slag. Fig. 49 shows the same variety of steel after it has been heated to 730° and quenched immediately in water. It contains troostite, ferrite, and martensite. Fig. 50 shows the structure produced by heating the same steel to 825°, allowing it to cool slowly from 825° to 720°, and then quenching it in water. The section after such treatment consists of martensite. Last, as regards this variety of steel, in fig. 51 the heating and quenching were effected at the same temperatures as in the case of fig. 50, but the steel was subsequently *tempered*, and the micro-section shows a confused structure without indicating the presence of definite constituents.

Figs. 52 and 53 were taken on micro-sections of steel which contain 1.24 to 1.5 per cent. of carbon. Fig. 52 consists mainly of pearlite. M. Osmond informed me that in the portion actually photographed the percentage of carbon probably fell below 1.24 per cent., as free cementite was absent, but it may be that the steel had not been cooled with sufficient slowness from a high

temperature. In fig. 53, steel which has been cooled slowly, cementite and pearlite are both present.

Figs. 54 and 55 are very interesting. They represent steel containing from 1.5 to 1.6 per cent. of carbon—such a variety of steel, in fact, as would be produced by the ordinary operation of cementation. Fig. 54 represents a specimen which has been cooled in air, that is, more or less rapidly, but it has not been quenched, and contains cementite and sorbite, which in certain portions passes into pearlite, while fig. 55 has been heated and quenched at 1000° in iced water. It contains austenite and possibly some martensite. The austenite is the lighter constituent, the darker being probably martensite.

In all the cases represented in fig. 56 analysis would indicate the presence of precisely the same amount of carbon, 1.5 per cent. The series begins with a section revealing the structure of the metal when in the state of forged blister steel. This section is the circular disc in the centre of the series. In No. 1 the steel has been heated to 1000°, worked and slowly cooled. In it the carbide occurs in confluent masses, the groundwork being made up of alternate bands of iron and carbide, so that the structure resembles mother of pearl, the association being called "pearlite." In No. 2 the same steel has been heated to 850° and quickly cooled in air. The confluent masses have to some extent disappeared, and there is a groundwork of carbide in the distinct form, to which the name "sorbite" has been given. In No. 3 the same steel has been heated to 850° and quenched in water, and has thereby been "hardened," and the resulting structure is minutely acicular, the product being called "martensite." In No. 4 the interest deepens: the same steel has been heated to 1050°, and quenched, not in water, but in iced brine. The result is totally different from "martensite"; there are broad chevron-like bands of "martensite," enclosing lighter and much softer portions, to which the name of "austenite" was given by its distinguished discoverer, M. Osmond; but this result hardly prepares us for what happens when the steel is still further cooled by placing it in liquid air, thereby cooling it to -243°. The material, as No. 5 shows, swells up and becomes martensite or something very like it, forming a fern-like structure of singular beauty. In No. 6 the treatment has resulted in partial reversion to the original structure, but the metal has been quenched from a temperature near its melting-point, and what is known as a "burnt" steel is the product. No. 7 shows the result of annealing the original steel at a temperature of 650° for a long time, followed by slow cooling; the result is better developed bands of cementite,  $\text{Fe}_3\text{C}$ , and of the groundwork of pearlite, than in the specimen No. 1. Finally, by heating any of the specimens, except No. 6, to 850°, working them, and allowing them to cool slowly, the structure with

MICRO-SECTIONS OF DIFFERENT VARIETIES OF STEEL.

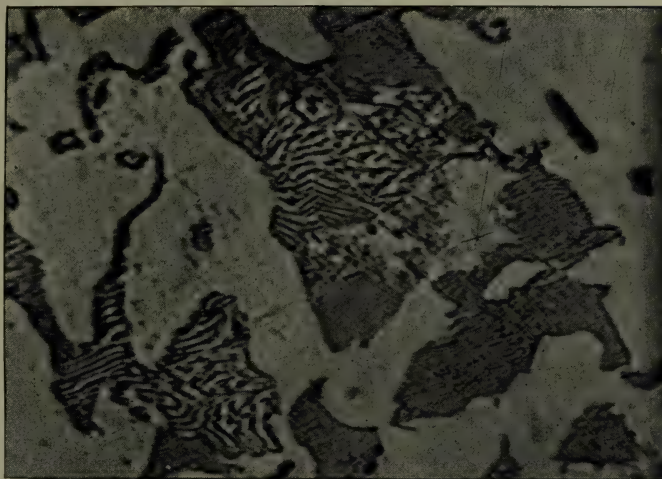


FIG. 48.—0.45 C. Steel. Annealed, showing Pearlite and Ferrite.

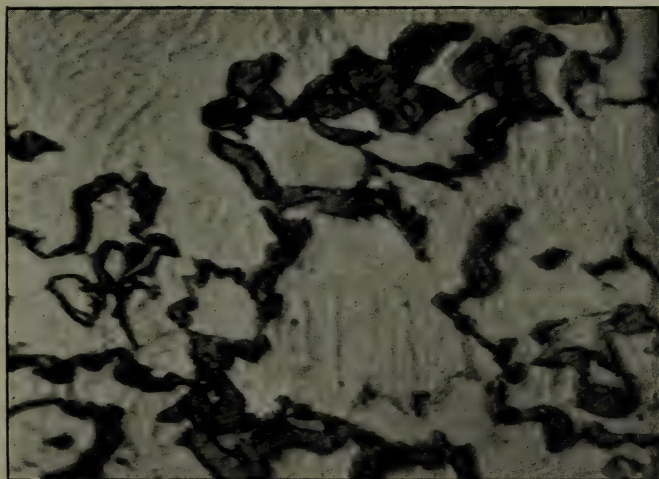
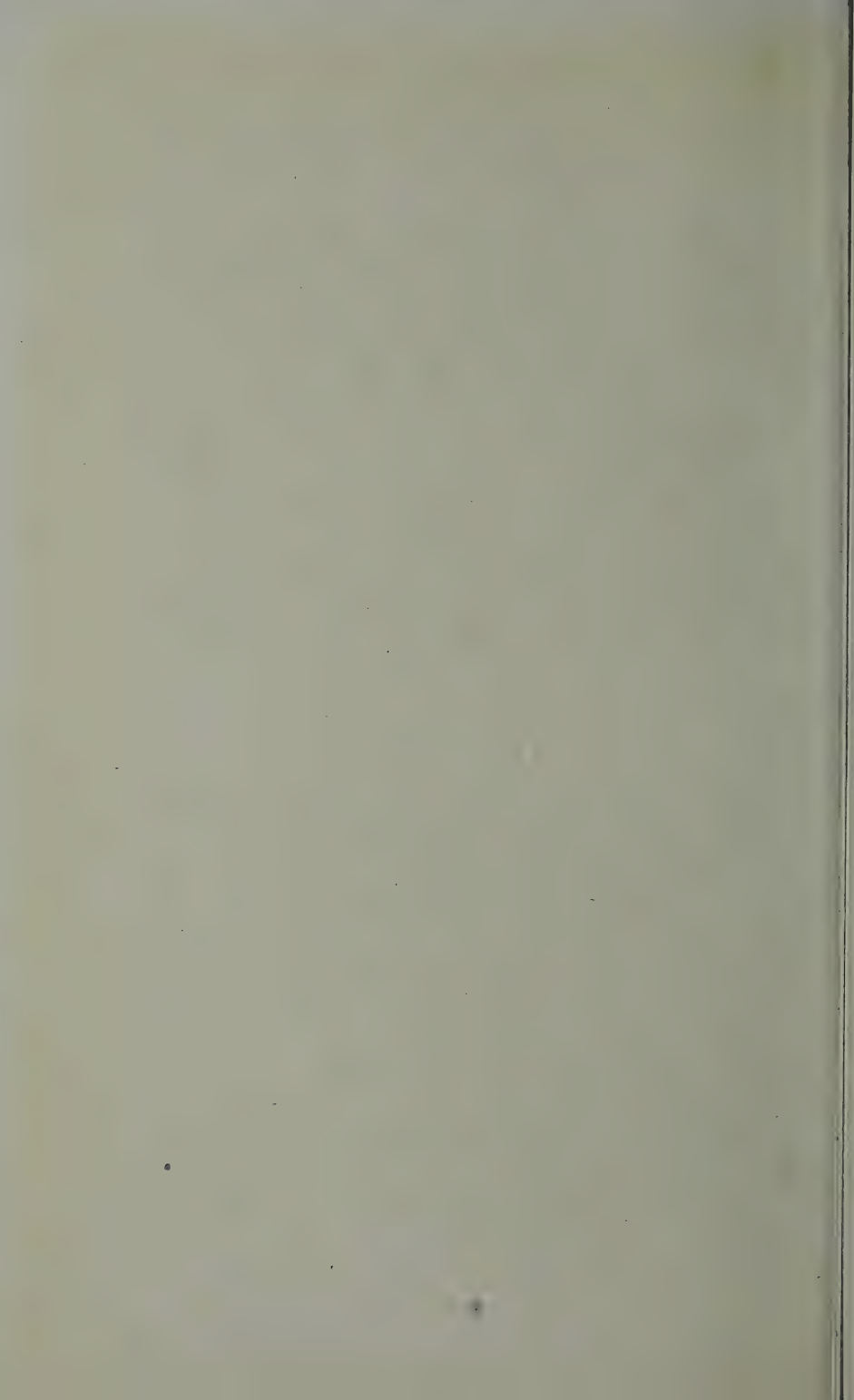


FIG. 49.—0.45 C. Steel. Quenched at 730° C., showing Troostite, Ferrite, and Martensite.





MICRO-SECTIONS OF DIFFERENT VARIETIES OF STEEL.

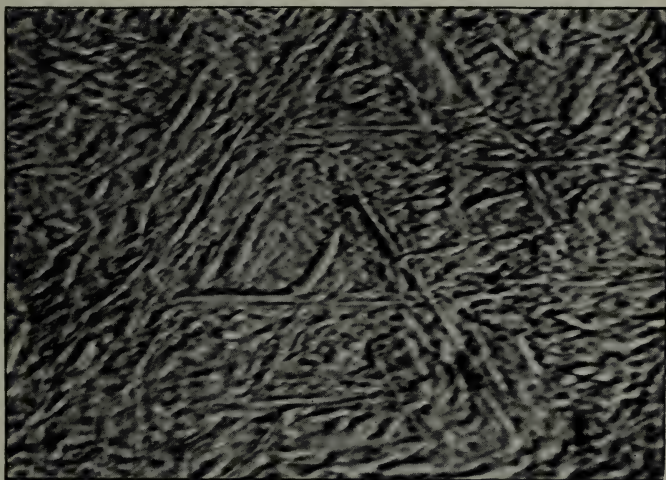


FIG. 50.—0.45 C. Steel. Quenched, showing Martensite.

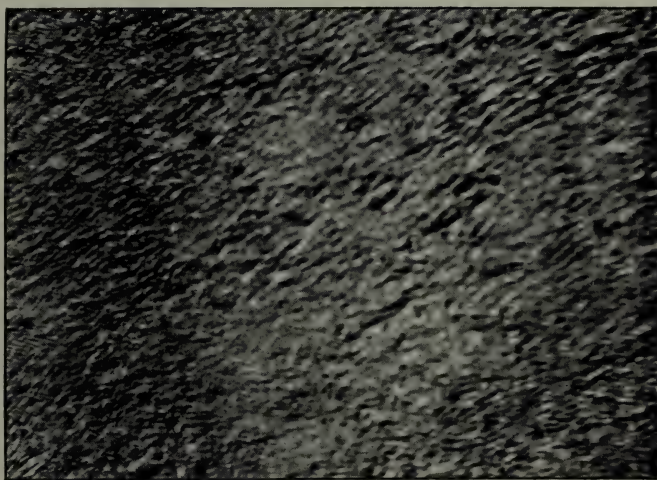


FIG. 51.—Same as above, but tempered after quenching.



MICRO-SECTIONS OF DIFFERENT VARIETIES OF STEEL.

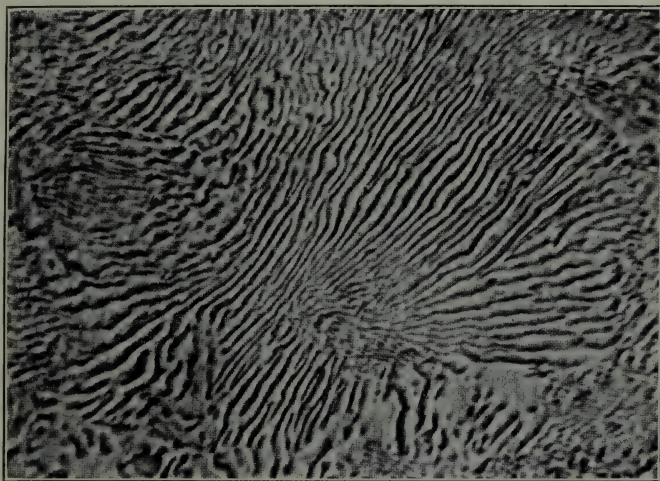


FIG. 52.—1.0 C. Steel, slowly cooled, showing Pearlite.

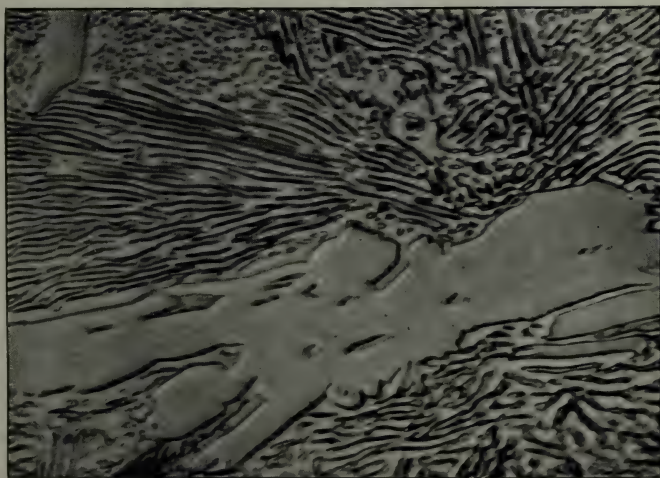
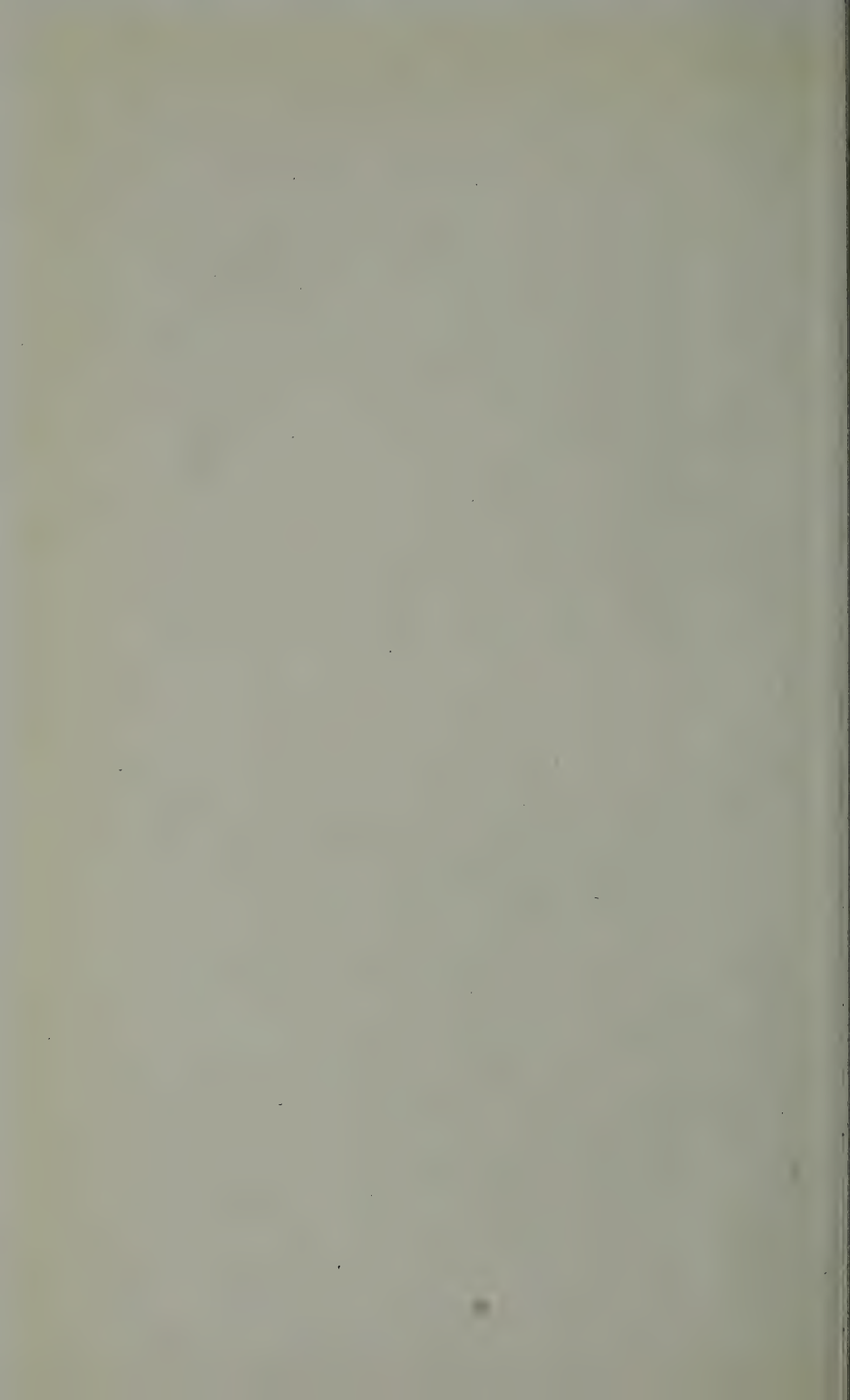


FIG. 53.—1.5 C. Steel, slowly cooled, showing Pearlite and Cementite.





MICRO-SECTIONS OF DIFFERENT VARIETIES OF STEEL.



FIG. 54 —1.5 C. Steel, cooled in air, showing Sorbitic Pearlite and Cementite.

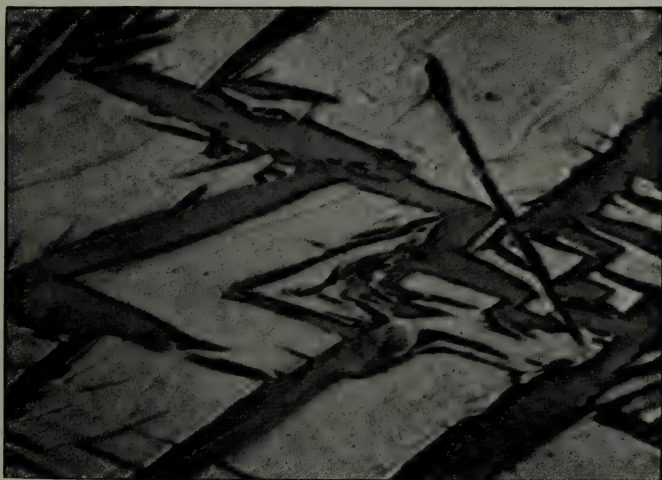
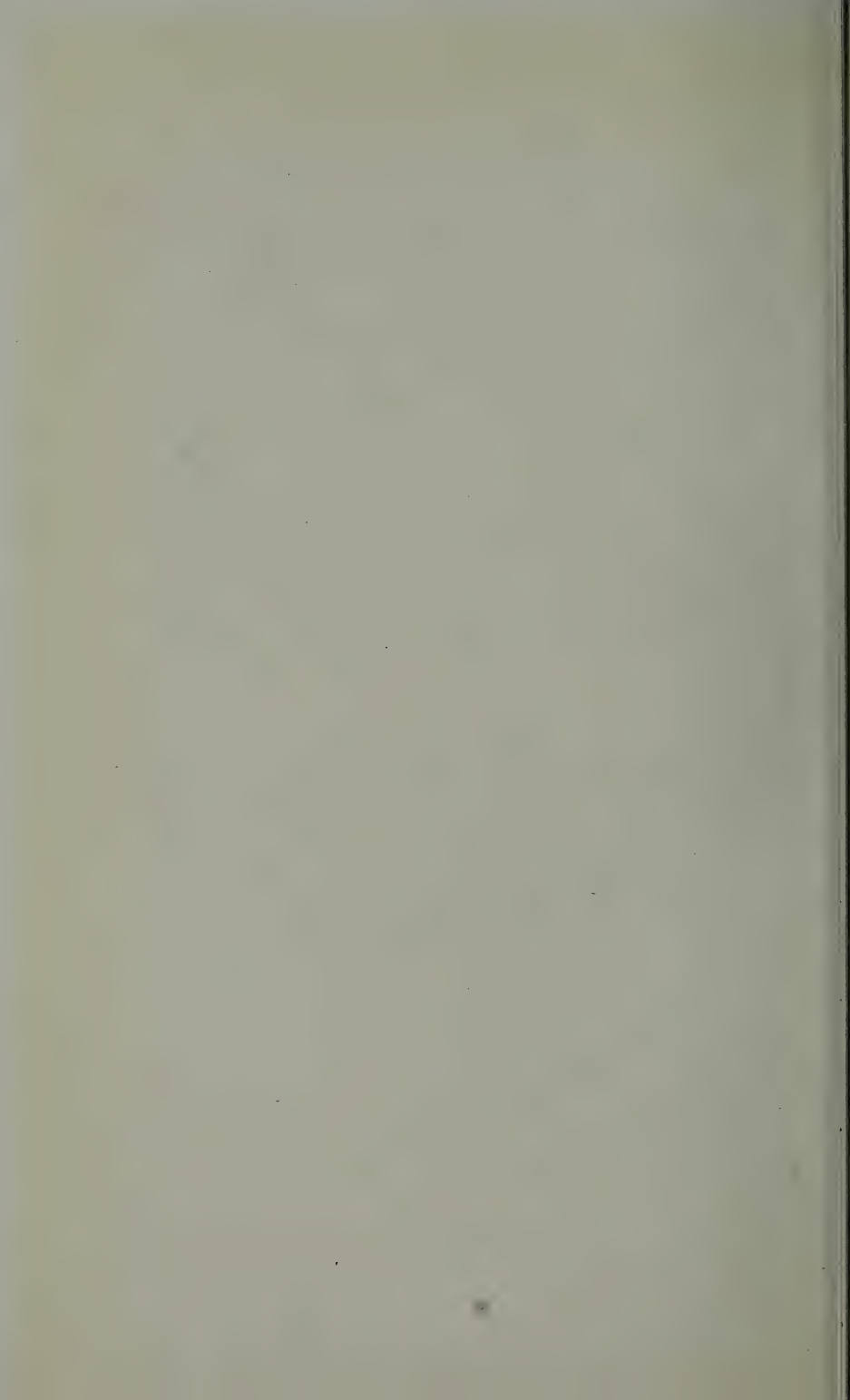


FIG. 55.—1.5 C. Steel. Quenched at 1000° in iced water, showing Austenite and Martensite.



MICRO-SECTIONS OF STEEL.

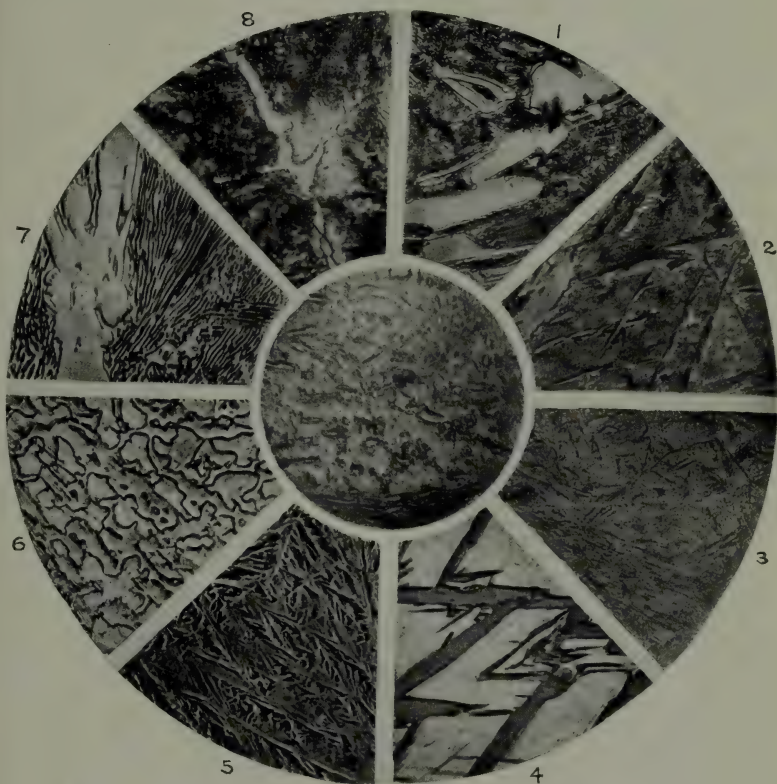
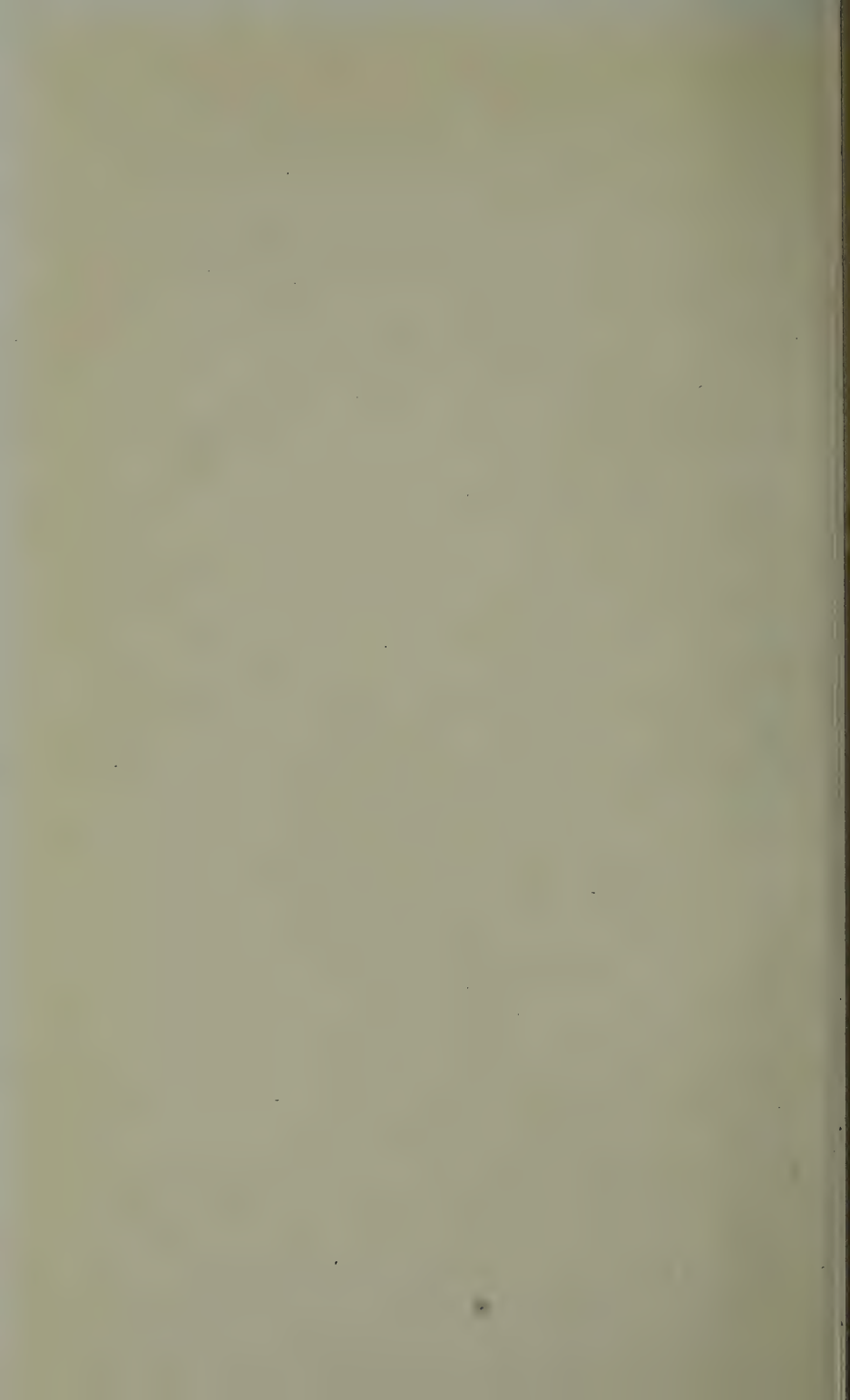


FIG. 56 -- Structures of 1.5 C. Steel. Centre, Forged Blister Steel.

1. Heated to  $1000^{\circ}$ , worked and slowly cooled.
2. Heated to  $850^{\circ}$  and cooled in air.
3. Heated to  $850^{\circ}$  and quenched in water.
4. Heated to  $1050^{\circ}$  and quenched in iced brine.
5. Effect of liquid air on structure 4.
6. Quenched near melting-point.
7. Annealed at  $650^{\circ}$  and slowly cooled.
8. From any except No. 6. Heated to  $850^{\circ}$ , worked and slowly cooled.





which we started in No. 1 is practically again obtained, as shown by No. 8.

For convenience, the specimens have been arranged as segments of a circle round the section representing the original mass of "cement" steel. The point to be borne in mind is that these complex and varied molecular changes have occurred, except in the case of No. 6, in the solid, for in no other case has the steel been raised to a higher temperature than  $1050^{\circ}$ , which is more than  $300^{\circ}$  below its melting-point.

It will, I think, be evident that photo-micrography affords most important information as to the constitution of steel.

As regards the modes of existence of carbon, M. Osmond has arranged the following very useful table which shows the

#### MODES OF EXISTENCE AND REACTIONS OF CARBON IN STEEL.

Description.		Formula.	Mode of occurrence in micro-section.	Results obtained by the respective methods of		
				Weyl.	Müller.	Eggertz.
Carbon, known as Cementation Carbon.	In fine plates.	$\text{Fe}_3\text{C}$ .	Pearlite.	Set free.	Set free.	Soluble, with a brown coloration.
	Free (segregated)?	$\text{Fe}_3\text{C}$ .	Free (segregated)?	Give a carbhydrate.	Set free, with possibly a certain amount of loss.	Soluble, with a brown coloration.
	Dissolved.	$\text{Fe}_3\text{C}$ .	Martensite. Sorbite. Austenite.			
Carbon, known as Hardening Carbon.		C ions.	Martensite. Troostite?	Partially gasified.	Gasified.	Gasified.

chemical properties of the different forms of carbon, other than graphite, which are met with in steel. It is the expression of a working hypothesis, fairly accounting for the facts which remain obscure in the chemical reactions of carbon in its various states. As M. Osmond<sup>1</sup> points out, this hypothesis admits, with Mr Sauveur, that there is a solution of carbide  $\text{Fe}_3\text{C}$ , which is at the same time the carbide of  $\beta$  iron of Mr Howe.

Iron containing about 0.9 per cent. of carbon is, in fact, at the saturation point for steel; and when the concentration of the carbide reaches a certain point, in consequence of the separation of the constituents which are in excess, either the carbide or the iron is isolated simultaneously at a constant temperature, giving rise to the pearly constituent of Sorby. "Pearlite" is the *solid*

<sup>1</sup> Discussion of a paper by Mr Sauveur, *Trans. American Inst. Mining Engineers*, Chicago meeting, Feb. 1897.

*eutectic* alloy of one of the forms of iron and of the carbide  $\text{Fe}_3\text{C}$ , and is generally called the “eutectoid,” to distinguish it from ordinary eutectics, the nature of which is explained on p. 232. A study of the admirable work of Ledebur<sup>1</sup> and Campbell,<sup>2</sup> the latter of whom has studied the condition of carbon in steel from the point of view of the complex hydrocarbons which are liberated when the metal is treated with acids, will show how complex the relations of carbon and iron really are; but the question arises—Does a change in the “mode of existence” of carbon in iron sufficiently explain the main facts of hardening and tempering? It is possible to obtain by rapid cooling from a certain temperature, steel which is perfectly soft, although analysis proves that the carbon is present in the form which has been recognised as “hardening carbon.” No doubt in the hardening of steel the carbon changes its mode of existence; but some other theory must be sought which will explain all the facts, and in order to do this it is necessary to turn to the behaviour of the iron itself.

In approaching this portion of the subject, a few elementary facts relative to the constitution of matter must be recalled, and in doing so a brief appeal to history must again be made. It is universally accepted that metals, like all elements, are composed of atoms of definite weights and volumes grouped in molecules. In order actually to transmute one metal into another it would be necessary to discover a method of attacking, not the molecule, but the *atom*, and of changing it, and this, so far as is known, has not yet been done; but it is possible, by influences which often appear to be very slight, to change the relations of the molecules to each other, and to alter the arrangement or distribution of the *atoms* within the molecules, and by varying, in this sense, the molecular arrangement of certain elements, they may be made to pass into states which are very different from those in which we ordinarily know them. Carbon, for instance, when free, or when associated with iron, may readily be changed from its diamond form to the graphitic state, though the converse change is much more difficult.

Sulphur, again, best known as a hard, brittle, yellow solid, may be prepared and maintained for a little time in the form of a brown viscous mass, but this latter form of sulphur soon passes spontaneously and slowly at the ordinary temperature, and instantaneously at  $100^\circ$ , to the solid octahedral yellow modification with evolution of heat. The viscous form of sulphur is an allotropic modification of that element. There are some well-known cases of allotropy in metals, and when they do occur they give rise to problems of vast industrial importance. Such

<sup>1</sup> *Stahl und Eisen*, vol. viii. (1888), p. 742; and *Journ. Iron and Steel Inst.*, 1893, part ii.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1899, ii. p. 223.

molecular changes in metals are sometimes produced by the addition of a small quantity of foreign matter, and it would appear that the molecular change produced by the action of *traces* upon *masses* is a widespread principle of nature, and one which was recognised at the dawn of the science of chemistry, even in the seventh century, but distorted explanations were given of well-known facts, and gave rise to entirely false hopes. But students would do well to bear in mind that it is the same story now as in mediæval times; the single grain of powder which Raymond Lully said would transmute millions of its weight of lead into gold, the single grain of stone that Solomon Trismosin thought would secure perpetual youth, had their analogues in the small amount of plumbago which, to Bergman's astonishment, in the eighteenth century, converted iron into steel. By his time it was recognised that the right use of alchemy consisted in the application of its methods to industry, and we still wonder at the minuteness of the quantity of certain elements which can profoundly affect the properties of metals. The statements are true, and are not derived from poetical literature, early or late. There is no need to fear the taunt of Francis Bacon,<sup>1</sup> that "sottishly do the chymics appropriate the fancies and delights of poets in the transformation of bodies to the experiments of their furnaces"; for although it may not be possible to *transmute* metals, it is easy so to *transform* them by very slight influences that, as regards special service required from them they may behave either usefully or entirely prejudicially.

The question at once suggests itself—Can iron behave in a similar manner: is an allotropic form of iron known? Joule afforded experimental evidence for an affirmative answer to this question many years ago by communicating to the British Association in 1850 a paper on some amalgams. The result of his experiments, published in detail later,<sup>2</sup> in a paper which has been sadly neglected, showed that iron released from its amalgam with mercury is chemically active, as it combines readily with the oxygen of the air at the ordinary temperature, and he claims that the iron so set free is allotropic; but Joule did much more than this. Magnus has shown (1851) that the thermo-electric properties of hard and of soft steel and iron differ. Joule, in a paper on some thermo-electric properties of solids, incidentally shows that the generation of a thermo-electric current affords a method of ascertaining the degree of carburisation of iron, and he appeals to the "thermo-electricity of iron in different states" as presenting a "fresh illustration of the extraordinary physical changes produced in iron by its conversion into steel," and he adds the expression of the belief "that the excellence of the

<sup>1</sup> Preface to the *Wisdom of the Ancients*.

<sup>2</sup> "On some Amalgams," *Mem. Lit. Phil. Soc. Manchester*, vol. ii. [3], p. 115.



latter metal might be tested by ascertaining the amount of change in thermo-electric condition which can be produced by the process of hardening."<sup>1</sup> It is by a thermo-electric method that the views as to the existence of iron in allotropic forms have been confirmed.

Jullien seems to have inclined to the view that iron is allotropic in his *théorie de la trempe*,<sup>2</sup> published in 1865, but he cannot be said to have done much beyond directing attention to the importance of hardening and tempering steel.

The next step was made in Russia in 1868. Chernoff showed that steel could not be hardened by rapid cooling until it had been heated to a definite temperature, to a degree of redness which he called *a*. Then, in 1873, Professor Tait<sup>3</sup> used this expression in a Rede Lecture delivered at Cambridge: "It seems as if iron becomes, as it were, a different metal on being raised above a certain temperature; this may possibly have some connection with the ferricum and ferrosium of the chemists." He also published his now well-known "first approximation to a thermo-electric diagram," which is of great interest in view of recent work. At about this time those specially interested in this question remembered that Gore<sup>4</sup> had shown that a curious molecular change could be produced by heating an iron wire. Barrett repeated Gore's experiment, and discovered that as an iron wire cools down it suddenly *glows*, a phenomenon to which he gave the name *recalcescence*, and these investigations have been pursued and developed in other directions by many skilful experimenters.<sup>5</sup> In 1879 Wrightson called attention to the abnormal expansion of carburised iron at high temperatures.

The next point of special importance appears to be that recorded by Barus, who, by a thermo-electric method, showed, in an elaborate paper published in 1879,<sup>6</sup> that "the hardness of steel does not increase continuously with its temperature at the moment of sudden cooling, but at a point lying in the dark-red heat state" a maximum hardness may be attained by rapid cool-

<sup>1</sup> *Phil. Trans.*, vol. cxlix. (1859), p. 95.

<sup>2</sup> *Annexe au Traité de la Métallurgie du Fer*, 1865.

<sup>3</sup> *Nature*, vol. viii. (1873), pp. 86, 122; and *Trans. Roy. Soc. Edin.*, vol. xxvii. (1873), p. 125.

<sup>4</sup> Gore, *Proc. Roy. Soc.*, vol. xvii. (1869), p. 260. Barrett, *Phil. Mag.*, vol. xlv. (1873), p. 472.

<sup>5</sup> G. Forbes, *Proc. Roy. Soc. Edin.*, vol. viii. (1874), p. 363. Norris, *Proc. Roy. Soc.*, vol. xxvi. (1877), p. 127. Tomlinson, *Phil. Mag.*, vol. xxiv. (1887), p. 256; vol. xxv. (1888), pp. 45, 103, and 372; vol. xxvi. (1888), p. 18. Newall, *ibid.*, vol. xxiv. (1887), p. 435; vol. xxv. (1888), p. 510. Fourth and Fifth Reports to Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1897, p. 31; 1899, p. 35. Carpenter and Keeling, *Journ. Iron and Steel Inst.*, 1904, i. p. 224. Rosenhain, *Proc. Physical Soc.*, 1907. Lambert, *Journ. Iron and Steel Inst.*, 1908, part i.

<sup>6</sup> Barus, *Phil. Mag.*, vol. viii. (1879), p. 341.



ing. Brief reference will again be made to the remarkable series of papers published by Barus and Strouhal,<sup>1</sup> embodying the results of laborious investigations, to which but scanty justice can be done here; and finally, in 1886, Pionchon<sup>2</sup> showed that at a temperature of 700° the specific heat of iron is altogether exceptional, and Le Chatelier<sup>3</sup> detected that at 700° a change occurs in the curve representing the electromotive force of iron, both experimenters concluding that they had obtained evidence of the passage of iron into an allotropic state. Osmond<sup>4</sup> then made the observations of Gore and Barrett the starting-point of a fresh inquiry. Bearing in mind the fact that molecular change in a body is always accompanied with evolution or absorption of heat, which is, indeed, the surest indication of the occurrence of molecular change, he studied, with the aid of a chronograph, what takes place during the slow cooling and the slow heating of masses of iron or steel, using as a thermometer to measure the temperature of the mass a thermo-electric couple of platinum, and of platinum containing 10 per cent. of rhodium, converting the indications of the galvanometer into temperatures by Tait's formulæ.

Figs. 57 and 58 show the actual mode of conducting the experiments. F, fig. 57, is a piece of steel into which a platinum and platinum-rhodium couple  $tt'$  is fixed. It is enclosed in a glazed porcelain tube, and heated to bright redness in the furnace

<sup>1</sup> "Hardness (Temper), its Electrical and other Characteristics," Barus, *Phil. Mag.*, vol. vii. (1879), p. 341; *Wied. Ann.*, vol. vii. (1879), p. 383. Strouhal and Barus, *ibid.*, vol. xi. (1880), p. 930; *ibid.*, vol. xx. (1883), p. 525. "Hardness and Magnetisation," *ibid.*, vol. xx. (1883), pp. 537, 662. "Density and (Internal) Structure of Hard Steel and of Quenched Glass," Barus and Strouhal, *American Journ.*, vol. xxxi. (1886), p. 386; *ibid.*, p. 439; *ibid.*, p. 181. "Temper and Chemical Composition," *ibid.*, vol. xxxii. (1886), p. 276. "Temper and Viscosity," *ibid.*, p. 444; *ibid.*, vol. xxxiii. (1887), p. 20. Barus, *ibid.*, vol. xxxiv. (1887), p. 1; *ibid.*, p. 175. These papers, systematically discussed and enlarged, are embodied with new matter in the Bulletins of the United States Geological Survey—viz. *Bull.* No. 14 (1885), pp. 1-226; *Bull.* No. 27 (1886), pp. 30-61; *Bull.* No. 35 (1886), pp. 11-60; *Bull.* No. 42 (1887), pp. 98-131. The later literature of the subject is very voluminous. Arnold, *Proc. Inst. Civil Engineers*, vol. cxxiii. (1895-6), p. 127. Sauveur, *Trans. Am. Inst. Mining Engineers*, vol. for 1896. This paper was elaborately discussed at the subsequent meeting of the Institute in 1897. Le Chatelier, *Comptes Rendus*, cxxxvi. pp. 664-667. Demozay, *Journ. Iron and Steel Inst.*, 1907, iii. 144.

<sup>2</sup> *Comptes Rendus*, vol. cii. (1886), pp. 675 and 1454.

<sup>3</sup> *Ibid.*, vol. cii. p. 819.

<sup>4</sup> "Théorie cellulaire des Propriétés de l'Acier," *Ann. des Mines*, vol. viii. (1885), p. 5. *Transformations du Fer et du Carbone*, Paris, Baudoin et Cie., 1888. "Études Métallurgiques," *Ann. des Mines*, Juillet-Août, 1888. "Sur les nouveaux Procédé de Trempe," Mining and Metallurgical Congress, Paris, 1889; *Journ. Iron and Steel Inst.*, No. 1 (1890), p. 38. "On the Critical Points of Iron and Steel," *Journ. Iron and Steel Inst.*, 1890, i. p. 38; "Transformations allotropiques dans les Fers et Aciers," *Comptes Rendus*, vol. ciii. pp. 743 and 1135; vol. civ. p. 985; vol. cvi. p. 115; vol. cx. pp. 242, 346; vol. cxii. p. 578; vol. cxiii. p. 474; vol. cxviii. p. 532.

S (fig. 58). This tube T may be filled with any gaseous atmosphere. C is a bulb filled with chloride of calcium. The metal under examination is slowly cooled down. The wires from the thermo-couple pass to the galvanometer G. The rate of cooling of the mass, as indicated by the movement of a spot of light from the galvanometer mirror M, on the screen R, is recorded by a chronograph. The source of light is shown at L.

The curves given in the diagram, fig. 59, show how the rate of movement of the spot of light varies with different samples of steel. The stoppage of the movement of the spot of light of course indicates the evolution of heat from the cooling mass of steel F (fig. 57).



FIG. 57.

In fig. 59 the temperatures through which a slowly cooling mass of iron or steel passes are arranged along the horizontal line, and the intervals of time during which the mass falls through a definite number (6.6) of degrees of temperature are shown vertically by ordinates. See what happens while a mass of electro-deposited iron (shown by a dotted line), which is as pure as any iron can be, slowly cools down. From  $1200^{\circ}$  to  $870^{\circ}$  it falls uniformly at the rate of about  $2.2^{\circ}$  a second, and the intervals of temperature are plotted as dots at the middle of the successive points of the intervals. When the temperature falls down to  $858^{\circ}$  there is a sudden arrest in the fall of temperature; the indicating spot of light, instead of falling at a uniform rate of about  $2^{\circ}$  a second, suddenly takes 26 seconds to fall through an interval of temperature which hitherto and subsequently only occupies about 6 seconds. The diagram (fig. 59) shows what actually happens when the iron contains carbon in the proportion required to constitute it mild steel (indicated by a thin continuous line, fig. 59); there is not one, but there are two such breaks in the cooling, and both breaks occur at a different temperature from that at which the break in pure iron occurred. As the proportion of carbon increases in steel, the first break in cooling travels more and more to the right, and gradually becomes confounded with the second break, which, in steel containing much carbon, is of long duration, lasting as much as 76 seconds in the case of steel containing 1.25 per cent. of carbon (thick continuous line, fig. 59).

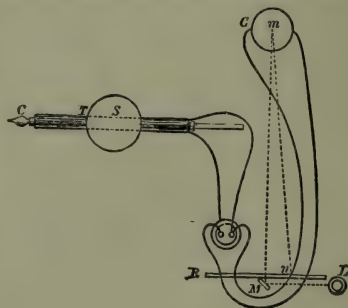


FIG. 58.

Now, it may be urged, as the presence of carbon has evidently an influence on the cooling of steel when left to itself, may it not affect molecular behaviour during the rapid cooling which is essential to the operation of hardening? It is known that the carbon during rapid cooling is retained in the state in which it is dissolved in the iron as carbide; it is also known that during slow cooling this dissolved carbide can separate itself from the iron so as to assume the form in which it occurs in soft steel. This second arrestation in the fall of the temperature corresponds to the recalescence of Barrett, and is caused by the reheating of the wire by the heat evolved when carbon leaves its state of solution and truly combines with the iron.

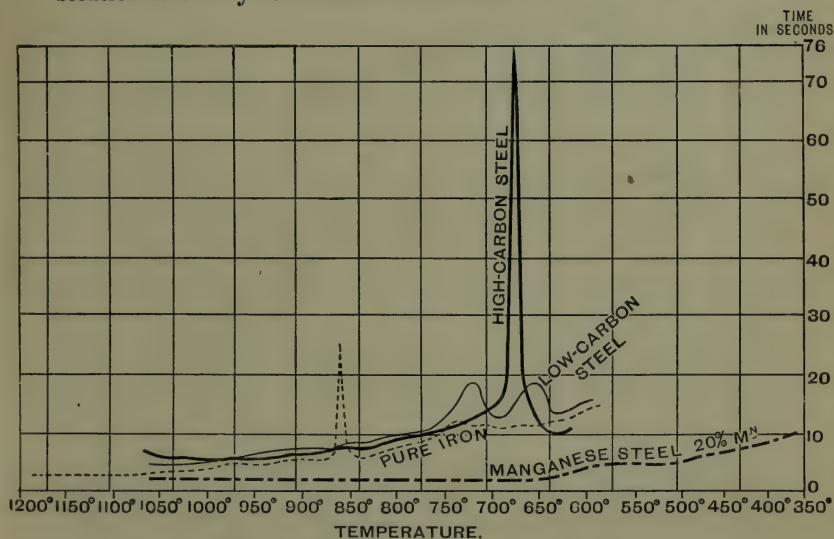


FIG. 59.

If it is hoped to *harden* steel, it must clearly be rapidly cooled before this combination of carbon and iron has taken place, or it will be too late to keep the carbon as hardening carbon. But what does the first break in the curves mean? It will be seen that it occurs in electrolytic iron, which is free from carbon; it must, then, indicate some molecular change in iron itself, accompanied with evolution of heat, a change with which carbon has nothing whatever to do, for no carbon is present, and Osmond argues thus:—There are two kinds of *iron*, the atoms of which are respectively arranged in the molecules so as to constitute *hard* and *soft iron*, quite apart from the presence or absence of carbon. In red-hot iron the mass may be soft, but the molecules are hard: let this be called  $\beta$  iron: cool such red-hot pure iron,



whether quickly or slowly, and it becomes soft; it passes to the  $\alpha$  soft modification, there is nothing to prevent its doing so. It appears, however, that if carbon is present, and the metal be rapidly cooled, the following result is obtained:—A certain proportion of the molecules are retained in the form in which they existed at a high temperature in the hard form, the  $\beta$  modification, and hard *steel* is the result.

In varieties of steel which contain less than 0.35 per cent. of carbon, there are three clearly shown main points of arrest in the cooling metal; and for these Osmond has given us a convenient notation: Ar, 3 occurs at 890°, Ar, 2 occurs at 760°, Ar, 1 occurs at 690°. (Round numbers have been given for the sake of clearness.)

There is, however, one other question of much importance to be considered. M. Osmond found that the appearance of magnetism in iron coincides exactly with the middle point in cooling-steel, that is, with the arrest in the evolution of heat from a cooling mass which is noted at 760° C. Now that it is demonstrated that the first arrest (about 890) and the second one (760) are independent, it seems clear that there must be three allotropic forms of iron instead of two—namely, the form  $\alpha$  existing at temperatures below Ar, 2, the form  $\beta$  between Ar, 2 and Ar, 3, and the form  $\gamma$  above Ar, 3. What parts respectively played by  $\beta$  iron and by  $\gamma$  iron in the hardening of steel, and in the properties of manganese-steels and nickel-steels, have been indicated by M. Osmond in his contribution to the discussion of Mr Sauveur's paper to which reference has already been made.<sup>1</sup> The question is too complicated for brief discussion in this volume.

From the engineer's point of view, the most interesting information which the pyrometer (described on p. 176) has as yet afforded is connected with the detection of molecular changes which give rise to internal stresses. It is evident that the occurrence of molecular changes must be of vital importance when the metal is subjected at high temperatures to mechanical operations such as rolling or forging. The question naturally arises—Do the molecular changes in the iron take place at one moment throughout the mass of metal?—that is, is the rate of cooling approximately uniform throughout the mass? Or does the external portion of a hot ingot cool so much more rapidly than the centre as to allow the molecular changes in the iron, and the alterations in the relation between the carbon and the iron, to become complete near the surface long before they take place in the interior of the mass? The experimental difficulties in the way of obtaining information upon these points have hitherto appeared to be insuperable; but the pyrometric method used in this research, in conjunction with the evidence of photo-micrography, affords

<sup>1</sup> *Trans. American Mining Engineers*, Chicago meeting, 1897.



most important evidence, as a brief description of the following experiments will show.

If the steel be allowed to cool under pressure (the student must consult the original memoir<sup>1</sup> to see how this was effected), it will be found that the point of recalescence is lowered, as will be seen by reference to the curves (fig. 60).

The sample of steel contained 0.9 per cent. of carbon, and when cooled in air without pressure recalescence took place at close upon 690°. In two experiments shown, respectively dotted and continuous lines marked "30 tons per square inch," the point of recalescence was sensibly lowered by that amount of pressure. When the ingot was quenched in water the recalescence point fell to 300°. As regards the other source of evidence, sections taken from different parts of an ingot or forging show a gradual transition in the appearance of the micro-structure from the outer

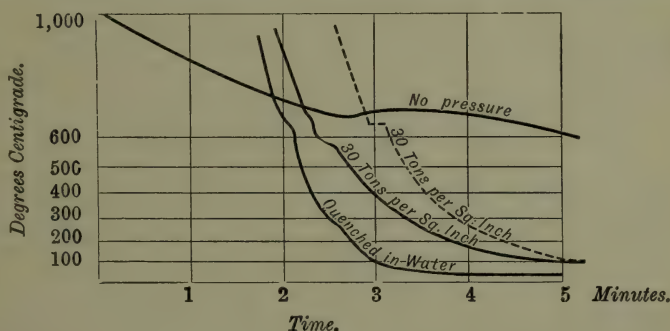


FIG. 60.

and quickly cooled portions to the inner and more slowly cooled portions.

Barus<sup>2</sup> has pointed out that since most metals can be hardened by straining, it would follow that there should be  $\alpha$  and  $\beta$  varieties in all cases, even though a molecular change corresponding to recalescence has only been observed in the case of a few metals. He believes, moreover, that there is reason to be urged in favour of this extreme view. This question has since received careful consideration by Howe.<sup>3</sup> The existence of molecular change in iron may be illustrated by the following experiment:—Take a bar of steel (fig. 61) containing much carbon. In such a variety of steel, the molecular change of the iron itself, and the change in the relations between the carbon and the iron, would occur at nearly the same moment. Heat this bar to red-

<sup>1</sup> *Inst. Mech. Eng.*, part ii., 1893, p. 125.

<sup>2</sup> *Nature*, vol. xli. (1890), p. 369.

<sup>3</sup> *Journ. Iron and Steel Inst.*, 1895, ii. p. 258.

ness, one end of the red-hot bar being firmly fixed (fig. 61), and sling a weight *not sufficient to bend it* to the free end, which is lengthened by the addition of a reed to magnify any motion that may take place. As the bar is red-hot, it ought to be at its softest when it is freshly withdrawn from the furnace, and if the weight was ever to have power to bend it, it would be then; but, in spite of the rapidity with which such a thin bar cools down in the air and becomes rigid, points of molecular weakness come when the iron changes from  $\beta$  to  $\alpha$ , and the carbon passes out of solution and forms carbide,  $\text{Fe}_3\text{C}$ ; at that moment, at a temperature much below that at which it is withdrawn from the furnace, the bar will begin to bend. It has been found experimentally that this is the point at which, according to Osmond's theory, molecular change takes place. Coffin takes advantage of this fact to straighten distorted steel axles.<sup>1</sup>

Barus<sup>2</sup> traces the connection of this singular minimum of the viscosity of hot iron and the interpretation given of Maxwell's theory of viscosity, and he points out that "when iron passes

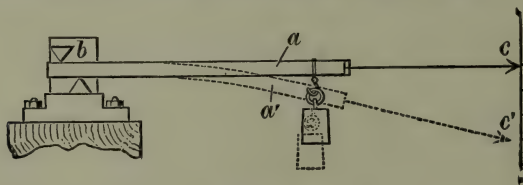


FIG. 61.

through the temperature of recalcence, its molecular condition is for an instant almost chaotic. This has now been abundantly proved by Hopkinson. The number of unstable configurations, or, more clearly, the number of configurations made unstable because they are built up of disintegrating molecules, is therefore at a maximum. It follows that the viscosity of the metal must pass through a minimum. Physically considered, the case is entirely analogous to that of a glass-hard steel rod suddenly exposed to  $300^\circ$ . If all the molecules passed from Osmond's  $\beta$  state to his  $\alpha$  state together, the iron or steel would necessarily be liquid. This extreme possibility is, however, at variance with the well-known principles of chemical kinetics. The ratio of stable to unstable configurations cannot at any instant be zero. Hence the minimum viscosity in question, however relatively low, may yet be large in value as compared with the liquid state."

Sir W. Anderson urged his opinion that "when, by the agency of heat, molecular motion is raised to a pitch at which incipient

<sup>1</sup> *Trans. American Soc. Civil Engineers*, vol. xvi. (1887), p. 324.

<sup>2</sup> *Nature*, vol. xli. (1890), p. 369.

fluidity is obtained, the particles of two pieces brought into contact will interpenetrate or diffuse into each other, the two pieces will unite into a homogeneous whole, and we can thus grasp the full meaning of the operation known as 'welding.' It is, however, possible to obtain evidence of interchange of molecular motion, as has been so abundantly shown by Spring, even at the ordinary temperature, while in the case of steel it must take place far below incipient fluidity, indeed at a comparatively low temperature, as is shown by the following experiment on the welding of steel. Every smith knows how difficult it is to weld highly carburised hard tool steel, but if the ends of a newly fractured  $\frac{1}{8}$ -inch square steel rod *a* (fig. 62) are covered with platinum foil *b* so as to exclude the air, and if the junction is heated in the flame of a Bunsen burner *c*, the metal will weld, without pressure, so firmly that it is difficult to break it with the fingers, although the steel has not attained a red heat.<sup>1</sup>

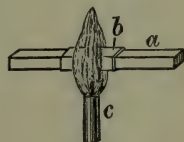


FIG. 62.

The question (partly considered in Chapter III.) now arises—What is the effect of the presence of other metals in steel? Take the case of manganese. This metal enables steel to harden very energetically, as is very well known. If much of it be present, 12 to 20 per cent., in iron, *no break whatever* is observed in the curve which represents slow cooling. (See line marked "Manganese Steel," fig. 59.) That is, the iron never shows such a change as that which occurs in other cooling masses of iron. Then such a material should be hard, however it is cooled. So it is. There is one other important point of evidence as to molecular change connected with the addition of manganese. Red-hot iron is not magnetic, and Hopkinson<sup>2</sup> showed in 1889 that the temperature of recalescence is that at which iron ceases to be magnetic. It may be urged that  $\beta$  iron cannot, therefore, be magnetised. Steel containing much manganese cannot be magnetised, and it is therefore fair to assume that the iron present is in the  $\beta$  form. Hadfield<sup>3</sup> has given metallurgists wonderful alloys of iron and manganese in proportions varying from 7 to 20 per cent. of manganese. Professor Ewing and others have specially examined the magnetic properties of this material, and Ewing concludes that "no magnetising force to which the metal is likely to be subjected, in any of its practical applications, would produce more than the most infinitesimal degree of magnetisation" in Hadfield's manganese steel. It has been seen that quantities of manganese above 7 per cent. appear to prevent the passage of  $\beta$  iron into the  $\alpha$  form. In smaller quantities,

<sup>1</sup> *Trans. American Soc. Mechanical Engineers*, vol. ix. (1888), p. 155.

<sup>2</sup> *Proc. Roy. Soc.*, vol. xlv. (1889), pp. 318, 455, and 457.

<sup>3</sup> *Proc. Inst. Civil Engineers*, vol. xciii., 1888, part iii. p. 1.



manganese seems merely to retard the conversion, and to bring the two loops of the diagram nearer together. With regard to the effect of other elements on steel, it need only be added that tungsten possesses the same property as manganese, but in a more marked degree. Chromium, on the contrary, enables the changes from hard  $\beta$  iron to soft  $\alpha$  iron to occur at a higher temperature than would otherwise be the case, and this may explain the extreme hardness of chromium steels when hardened in the same way as ordinary steels.

The disappearance of the magnetic properties of iron on heating is of much interest in relation to the allotropism of the metal. Gilbert appears to have been the first to demonstrate, in his treatise *de Magnete*, published in 1600, that red-hot iron is not magnetic; and nearly half a century later Sir Thomas Browne,<sup>1</sup> with frequent reference to Gilbert's work, states that masses of iron, "by the fire, omit whatsoever they had received from the earth or loadstone," and he gives evidence of being aware that what is now called the "magnetic permeability" of iron and steel is affected by heating and cooling the metal. These facts have been recognised as being of vital importance in modern research, and they derive new interest from the sharp identification of the loss of magnetism with the temperature at which a molecular change in the iron takes place, and from Hopkinson's discovery that an alloy of iron with 25 per cent. of nickel is magnetisable if it be previously cooled (by solid carbonic anhydride) to a very low temperature.

**Working of Steel.**—There are a few considerations relative to the actual working of steel which can but briefly be dealt with, notwithstanding their industrial importance. The points *a* and *b* adopted in the celebrated memoir of Chernoff, the temperatures at which the carbon changes its state during heating and cooling respectively, change in position with the degree of carburisation of the metal. It is useless to attempt to harden steel by rapid cooling if it has fallen in temperature below the point (in the red) *a*, and this is the point of "recalescence" at which the carbon combines with the iron to form carbide carbon; it is called *W* by Brinell.<sup>2</sup> In highly carburised steel, it corresponds exactly with the point at which Osmond considers that iron, in cooling slowly, passes from the  $\beta$  to the  $\alpha$  modification. Now with regard to the point *b* of Chernoff (or *W* of Brinell). If steel be heated to a temperature above *a*, but below *b*, it remains fine-grained, however slowly it is cooled. If the steel be heated above *b* and cooled, it assumes a crystalline granular structure whatever the rate of cooling may be. The size of the crystals, however, increases with the temperature to which the steel has been raised. The work

<sup>1</sup> *Pseudodoxia Epidemica; or Enquiries into Vulgar Errors*. 2nd edition, 1650, p. 45.

<sup>2</sup> *Stahl und Eisen*, 1885.



both of Chernoff and of Brinell had for its object the determination of the relations between the thermal treatment condition of the carbon and the fracture. The importance of knowing exactly what is likely to occur by varying the thermal treatment has since received wide recognition. One result of this is that in working steel the "finishing" temperature is now carefully considered. In the case of steel rails, Mr Robert Hunt<sup>1</sup> of Chicago places the finishing temperature as low as 1580° F. (860° C.).

Now the crystalline structure, which is unfavourable to the steel from the point of view of its industrial use, may be broken up by the mechanical work of forging the hot mass; and the investigations of Abel, of Maitland, and of Noble have shown how important "work" on the metal is. When small pieces of steel are quenched in oil from a high temperature they are hardened, but to a less extent than if water be used as the cooling agent; this partial hardening has a toughening effect on the metal, and the tendency to brittleness is far less marked than in the case of water quenching.<sup>2</sup> If the mass of metal is large, such as a propeller shaft or tube of a large gun, the change in the relations between the carbon and the iron, or true "hardening," produced by such oil treatment, is only effected *superficially*, that is, the hardened layer does not penetrate to any considerable depth, but the innermost parts are cooled more quickly than they otherwise would have been, and the development of the crystals, which would have assumed serious proportions during slow cooling, is arrested. It depends on the size of the quenched mass whether the tenacity of the metal is or is not increased, but its power of being elongated is considerably augmented. This prevention of crystallisation probably constitutes the great merit of oil quenching, which, as regards large masses of metal, is certainly not a true hardening process.

The effect of annealing remains to be dealt with. In a very complicated steel casting, the cast metal probably contains some of its carbon as hardening carbon, and the mass, which has necessarily been poured into the mould at a high temperature, is more or less crystalline. The effect of annealing is to permit the carbon to pass from the "hardening" to the "carbide" form, and incidentally to break up the crystalline structure, and, perhaps a matter equally important from a practical point of view, to relieve the stress set up due to unequal cooling. The result is that the annealed casting is more reliable; a test bar taken will give a higher elongation under work stress than one from the original casting. It would obviously be impossible to "work"—that is, to hammer—complicated castings; and the extreme importance of obtaining a fine crystalline structure by annealing, with the

<sup>1</sup> *Trans. Amer. Inst. Min. Eng.*, Feb. 1901.

<sup>2</sup> This was well shown in Prof. Akerman's celebrated paper on "Hardening Iron and Steel," *Journ. Iron and Steel Inst.*, 1879, part ii. p. 504.

strength which results from such a structure, has been abundantly demonstrated by Mr J. W. Spencer of Newcastle.

The effect of annealing and tempering is, in fact, very complicated, as is shown by the long series of researches which Barus and Strouhal have conducted. They consider that annealing is demonstrably accompanied by chemical change even at temperatures slightly above the mean atmospheric temperature, and that the "molecular configuration of glass-hard steel is always in a state of incipient change . . . a part of which change must be of a permanent kind." Barus considers<sup>1</sup> that glass-hard steel is constantly being spontaneously "tempered" at the ordinary temperature, which, he says, "acting on freshly quenched [that is, hardened] steel for a period of years, produces a diminution of hardness about equal to that of 100° C. acting for a period of hours."

The nature of the molecular change is well indicated in the long series of researches which led them to conclude that in steel "there is a limited interchange of atoms between molecules under stress, which must be a property common to solids if, according to Clerk-Maxwell's conception, solids are made up of configurations in all degrees of molecular stability."

Barus and Strouhal attach but little importance to the change in the relations between the carbon and the iron during the tempering and annealing of hard steel. They consider that in hardening steel the "strain once applied to steel is locked up in the metal in virtue of its viscosity"; tempering is the release of this molecular strain by heat.

Highly carburised steels harden very energetically by very slight modifications in thermal treatment, and it will be evident that a very hard material is unsuitable for industrial use if the conditions of its employment are such as to render it desirable that the material should stretch.

To turn to the class of steel which does not harden, it is certain that, although wrought iron passes almost insensibly into steel, there can be no question that, not merely the structural, but the molecular aggregation of even steel containing only  $\frac{2}{100}$  per cent. of carbon is profoundly different from that of wrought iron. The class of steel which was formerly employed for weapons and tools belonged to the highly carburised, readily hardening class. It was the "mild steel," containing but little carbon, which was destined to replace wrought iron; and when attempts were made to effect the general substitution of steel for iron, fears as to its character and trustworthiness unfortunately soon arose, so that from about the year 1860 until 1877 steel was viewed with suspicion. This can now be explained. Doubts as to the fidelity of steel, even when it was obtained free from entangled cinder, arose from ignorance of the fact that, on either side of a comparatively narrow thermal boundary, the physical

<sup>1</sup> *Phil. Mag.*, vol. xxvi. (1888), p. 209.

properties of iron and steel may vary greatly. The steel was "true" enough, but, from the point of view of the special duties to be entrusted to it, its fidelity depended largely on the heat treatment it had received. Artificers attempted to forge steel after it had cooled down below the point *a* of Chernoff at which recalescence occurs, and they often attempted to work highly carburised steel at insufficiently low temperatures.

**Classification of Steel.**—From the foregoing remarks, it will be evident that the use of steel depends largely upon its power of being hardened and tempered. At the same time it must not be imagined that all steel is hardened and tempered before use. The greater proportion of what is known as steel is used in the condition in which it leaves the rolls. This includes all mild steel used for structural purposes, boiler-plate, and steel rails. It may not be out of place, therefore, to indicate the way in which steel may be classified from the point of view of its industrial use, according to the amount of carbon it contains. Steels may be grouped under certain definite percentages of carbon, ranging from 0·1–1·5 per cent. Each class merges into the other, but the members at either end of the series vary very greatly. A sharp razor cannot be made from boiler-plate, and razor steel is unsuited for making a boiler that will resist high temperature when overheated.

The steel used for naval construction contains 0·15–0·2 per cent. of carbon. When steel faces are used for the armour-plates, the material contains 0·7–0·8 per cent. of carbon.

With regard to steel used in civil engineering, the most remarkable case is presented by the Forth Bridge. The steel of which the compression members of the structure are composed contains 0·23 per cent. of carbon and 0·69 per cent. of manganese. The parts subjected to extension do not contain more than 0·19 per cent. of carbon.<sup>1</sup>

Steel rails contain from ·35–·55 per cent. of carbon, and in this class slight variations in the amount of carbon are of considerable importance, as in certain climates a variation of 0·1 per cent. in the amount of carbon may be very serious. The great benefit which has accrued to the country from the substitution of more durable steel rails for the old wrought-iron ones may be gathered from the statement of Webb of Crewe, which shows that "the quantity of steel removed from the rails throughout the London and North-Western system by wear and oxidation is about 15 cwt. an hour, or 18 tons a day."

Gun-steel contains 0·3–0·4 per cent. of carbon, and it may contain 0·8 per cent. of manganese. It is in relation to gun-steel that oil hardening becomes very important. The oil tank of the Saint-Chamond Works (on the Loire) is 72 feet deep, and contains 44,000 gallons of oil, which is kept in circulation by rotary

<sup>1</sup> *Journ. Iron and Steel Inst.*, vol. ii. (1888), p. 94.



pumps to prevent the oil being unduly heated locally when the heated mass of steel is plunged into it.

The most formidable projectiles belong to the highly carburised class of steel. Shells contain 0·8–0·94 per cent. of carbon, and, in addition, some of these have up to 2 per cent of chromium. The firm of Holtzer showed in the Paris Exhibition a shell which pierced a steel plate 10 in. thick, and was found, nearly 800 yds. from the plate, entire and without flaw, its point alone being slightly distorted.

Lastly, reference must be made to the highly carburised steel used for the manufacture of dies. Such steel should contain 0·8 to 1 per cent. of carbon and little manganese. It is usual to water-harden and temper it to a straw colour, and a really good die will strike 40,000 coins of average dimensions without being fractured or deformed; and if the steel contain 0·1 per cent. too much carbon, it would not strike 100 pieces without cracking; and if it contained 0·2 per cent. too little carbon, it would probably be hopelessly distorted and its engraved surface destroyed in the attempt to strike a single coin.

The above examples will be sufficient to show how diverse are the properties which carbon confers on iron, but, as Faraday said in 1822, "it is not improbable that there may be other bodies besides charcoal capable of giving to iron the properties of steel." The strange thing is that it is not known with any certainty whether, in the absence of carbon, other elements do play the part of that metalloid in enabling iron to be hardened by rapid cooling. Take the case of chromium, for instance; chromium-carbon steels can, as is well known, be energetically hardened, but Busek<sup>1</sup> has asserted that the addition of chromium to iron in the absence of carbon does not enable the iron to be hardened by rapid cooling. Probably by employing the electrical method of heating adopted by Pepys a decision will be arrived at as to the hardening properties of elements other than carbon.

A few words must be devoted to the consideration of the colours which direct the artist in tempering or reducing the hardness of steel to any determinate standard. The technical treatises usually give, not always accurately, as Reiser<sup>2</sup> has shown, a scale of temperature ranging from 220° to 330°, at which various tints appear, passing from very pale yellow to brown-yellow, purples, and blues to blue tinged with green, and finally to grey. Barus and Strouhal point out<sup>3</sup> that it is possible that the colour of the oxide film may afford an indication of the temper of steel of far greater critical sensitiveness than has hitherto been supposed. How far time, temperature, and colour are correlated is uncertain.

That the colours produced are really due to oxidation was

<sup>1</sup> *Stahl und Eisen*, vol. ix. (1889), p. 728.

<sup>2</sup> *Das Härten des Stahles*, p. 78 (Leipzig, 1881). See also Loewenherz, *Zeitschrift für Instrumentenkunde*, vol. ix. (1889), p. 322.

<sup>3</sup> *Bull. U.S. Geo. Survey*, No. 27 (1886), p. 51.



shown by Sir Humphry Davy in 1813,<sup>1</sup> but the nature of the film has been the subject of much controversy. Barus points out that "the oxygen molecule does not penetrate deeper than a few thousand times its own dimensions," and that it probably passes through the film by a process allied to liquid diffusion. The permeable depth increases rapidly with the temperature until, at an incipient red heat, the film is sufficiently thick to be brittle and liable to rupture. A table of temperatures corresponding to colour tints is given by Howe.<sup>2</sup>

**Summary.**—Looking back over all the facts dealt with on the thermal treatment of steel, it will be evident that two sets of considerations are of special importance—(1) those which belong to the relations of carbon and iron, and (2) those which contemplate molecular change in the iron itself. The first of these has been deliberately subordinated to the second, although it would have been possible to have written much in support of the view that carburised iron is an alloy of carbon and iron, and to have traced, with Guthrie, the analogies which alloys, in cooling, present to cooling masses of igneous rocks. This view has been developed with much ability by Howe,<sup>3</sup> whose suggestion of mineralogical names such as "cementite," "pearlite," and "ferrite" for the various associations of carbon and iron is now generally adopted.

Such analogies present considerable interest, but the possibility of molecular change in the iron itself, which results in its passage into a distinctive form of iron, is at present an important subject for consideration, not merely in relation to iron, but as regards the wider question of allotropy in metals generally.

Many facts noted in spectroscopic work will, as Lockyer has shown, have indicated the high probability that the molecular structure of a metal like iron is gradually simplified as higher temperatures are employed. These various simplifications may be regarded as allotropic modifications.

The question of molecular change in solid metals demands continued and rigorous investigation. It is well known what important discoveries have been made in chemistry by the recognition of the fact that the elements act on each other in accordance with the great law of Mendeléef, which states that the properties of the elements are periodic functions of their atomic weights. There is little doubt but that it will be shown that the relation between small quantities of elements and the masses in which they are hidden is not at variance with the same law.

The future of steel will depend on the care with which the nature of the influence exerted by various elements on iron is

<sup>1</sup> Sir Humphry Davy, *Thomson's Ann. Phil.*, vol. i. (1813), p. 131, quoted by Turner, *Proc. Phil. Soc. Birmingham*, vol. vi. (1889), part ii.

<sup>2</sup> Howe, *Metallurgy of Steel*, p. 23 (1890).

<sup>3</sup> *Engineering and Mining Journal*, vol. xlvi. (1888), p. 131. See also *The Metallurgy of Steel*, vol. i. (New York, 1890), p. 165.

investigated, and by ascertaining the thermal treatment to which it may most suitably be subjected.

**Thermal Treatment of Industrial Alloys.**—Although the great changes made possible by slightly varying the thermal treatment of steel are not found to the same extent in non-ferrous alloys, yet it is recognised that very valuable properties may be induced in various alloys by correct heat treatment. The correct temperature for casting is an important point and has been studied by Longmuir,<sup>1</sup> who found, in the case of brasses and bronzes, that the tenacity, ductility, and contraction of area increase as the temperature of casting decreases from a high temperature to a fair casting heat, and that, on further cooling down before casting, a distinct fall in mechanical properties results. Gun-metal and Muntz metal cast at lower temperatures were found to be mechanically better than those cast at higher temperatures, whereas in the case of yellow and red brasses a high-temperature cast was found to be better than a low-temperature cast. The following table illustrates this point:—

Alloy.	No.	Casting Temperature.	Elastic Limit. Tons per Sq. In.	Maximum Stress. Tons per Sq. In.	Extension on 2 ins. Per cent.	Reduction of Area. Per cent.
Gun-metal .	{ 1	1173	6·468	8·376	5·5	4·23
	{ 2	1069	8·482	14·838	14·5	16·71
	{ 3	965	8·984	11·018	5·0	6·36
Yellow Brass	{ 1	1182	4·432	11·484	37·75	31·40
	{ 2	1020	3·974	12·713	43·00	35·66
	{ 3	850	4·150	7·447	15·00	15·25
Red Brass .	{ 1	1308	4·284	6·855	13·25	12·65
	{ 2	1073	4·263	12·649	26·00	30·28
	{ 3	1058	4·376	5·670	5·5	6·64
Muntz Metal	{ 1	1038	8·753	12·454	6·0	10·60
	{ 2	973	9·637	18·889	15·0	16·10
	{ 3	943	9·526	16·287	9·5	14·81

The importance of casting temperature is also illustrated by the following figures of an aluminium-copper alloy containing 4·63 per cent. of copper,<sup>2</sup> showing that the tenacity and ductility are greatly decreased by even small increases in the casting temperature:—

Casting Temperature.	Yield Point. Tons per Sq. In.	Ultimate Stress. Tons per Sq. In.	Elongation on 2 ins. Per cent.
650°	5·6	9·68	8·5
724	5·0	7·04	5·5
707	4·5	4·89	3·0

<sup>1</sup> *Journ. Iron. and Steel Inst.*, 1903, i. p. 457.

<sup>2</sup> *Proc. Inst. Mech. Eng.*, 1907, p. 92.

**Sand Casting and Chill Casting.**—The rate at which the metal cools down after casting is found to make a considerable difference in the mechanical properties of some alloys. In ordinary sand casting the metal cools down fairly slowly, whereas when a chill is introduced, in the form of an iron mould for casting, the cast solidifies much more quickly, especially on the surface, and valuable properties are thus induced. In the case of copper-aluminium alloys up to 9 per cent. of aluminium the chill castings gave somewhat better mechanical tests; and at the other end of the series, aluminium alloys containing up to 6 per cent. of copper, chill castings are superior to sand castings, both in strength and ductility.

**Effect of Annealing Alloys.**—The aluminium bronze containing 9·9 per cent. Al was found to be very sensitive to heat treatment,<sup>1</sup> the results of mechanical tests showing that profound changes take place between 300° and 400°; for after annealing at 300° the tests are practically the same as those of rolled bars, whereas after annealing at 400° there is shown a rise of nearly 100 per cent. in the elastic ratio, due to an increase in yield point and a decrease in ultimate stress, and it will be seen from the following table that the ductility has dropped almost to *nil*; the fractures also are found to be characteristically different. It is somewhat surprising that these changes in mechanical properties are not accompanied by differences in microscopic structure, the etched surface appearing very similar to that obtained with the rolled bar. On annealing at 800° and 900° there is a further loss of strength; the fracture becomes coarsely crystalline, and the etched surfaces of specimens heated in this range show considerable structural alterations.

EFFECT OF ANNEALING ALUMINIUM BRONZE (9·9 per cent. Al).

Treatment.	Yield Point. Tons per Sq. In.	Ultimate Stress. Tons per Sq. In.	Elastic Ratio.	Elongation, Per cent. on 2 ins.	Reduction of Area. Per cent.
Bar as rolled	14·8	38·1	·39	28·8	30·80
Annealed 1 hour at 300°	14·6	38·04	·38	27·0	33·06
"    "    400	23·4	31·69	·74	2·5	2·86
"    "    500	20·5	34·08	·60	9·5	13·11
"    "    600	15·7	31·74	·50	9·0	14·50
"    "    700	15·1	31·85	·48	9·0	11·25
"    "    800	12·7	26·23	·48	13·5	21·60
"    "    900	13·3	21·95	·61	6·0	8·76

<sup>1</sup> *Proc. Inst. Mech. Eng.*, 1907, p. 178.

**Effect of Quenching Aluminium Bronze at various Temperatures.**—When the alloy containing 9·9 per cent. Al is quenched in water from various temperatures above 600°, a rise in yield point and ultimate stress is obtained, with a corresponding fall in elongation and reduction of area, the results being most pronounced above 800°, as will be seen from the following table :<sup>1</sup>—

EFFECT OF QUENCHING ALUMINIUM BRONZE (9·9 per cent. Al).

Quenching Temperature.	Yield Point. Tons per Sq. In.	Ultimate Stress. Tons per Sq. In.	Elastic Ratio.	Elongation on 2 ins. Per cent.	Reduction of Area. Per cent.
600°	17·0	38·18	0·45	22·2	30·00
700	18·1	39·76	0·46	15·4	20·60
800	32·4	43·57	0·75	7·0	14·29
900	39·8	51·51	0·77	3·0	4·83

**Effect of Annealing Muntz Metal.**—The effect of annealing Muntz metal (Cu 60, Zn 40) at different temperatures and for different lengths of time has been studied by Bengough and Hudson,<sup>2</sup> and from their paper the following table is copied, showing that the general effect of annealing this alloy is to reduce the ultimate stress and increase the elongation.

Temperature of Annealing.	Time.	Ultimate Stress. Tons per Sq. In.	Elongation on 2 ins. Per cent.
As cast	...	23·4	17·1
As rolled	...	30·2	37·7
310°	7 hours	28·6	43·0
335	7 days	27·4	45·1
410	7 hours	27·4	48·0
490	7 "	26·1	56·0
540	7 "	24·4	57·7
685	7 "	23·5	53·5

**Effect of Mechanical Work on the Properties of Alloys.**—The mechanical tests of some alloys are very much improved by work, *e.g.* rolling or drawing, with or without annealing, and a very good example of this is found in the case of aluminium alloys containing from 0·8 per cent. Cu ; all these alloys roll well, and from 0·4 per cent. Cu they draw sound also. These alloys

<sup>1</sup> *Proc. Inst. Mech. Eng.*, 1907, p. 173.

<sup>2</sup> *Journ. Soc. Chem. Ind.*, xxvii., 1908, pp. 43 and 654.



require a considerable amount of mechanical work in order to get the full value of their inherent properties, and the following table<sup>1</sup> illustrates the beneficial effect on an alloy containing 3·76 per cent. Cu:—

Conditions.	Yield Point. Tons per Sq. In.	Ultimate Stress. Tons per Sq. In.	Elastic Ratio.	Elongation on 2 ins. Per cent.	Reduction of Area.
Chill casting . . .	5·4	9·60	0·56	10·5	21·46
1½-in. rolled bar . .	9·0	16·83	0·54	20·0	38·21
1½-in. " " " "	11·6	17·00	0·68	21·0	49·76
1½-in. bar drawn with annealing . . .	15·5	16·90	0·92	8·0	21·79
2½-in. bar drawn without annealing }	18·5	20·00	0·92	7·5	20·84

The improvements effected in yield point and in the case of the 1½ and 1⅜ in. rolled bars in reduction of area are particularly noticeable and important; and as this is an alloy whose specific gravity is only 2·79, it may be found very useful where a combination of lightness and strength is desired, and is worth further investigation.

#### BIBLIOGRAPHY OF WORK ON THE THERMAL TREATMENT OF STEEL.

- Brinell.—*Stahl und Eisen*, 1885 (reproduced in *Metallographist*, vol. ii., No. 2).
- Howe.—*Metallurgy of Steel, Hardening of Steel* (*Journal of the Iron and Steel Inst.*, 1895, ii. p. 258).
- Hadfield.—*Heat Treatment of Manganese Steel and its Bearing on Carbon Steel* (*Journal of the Iron and Steel Inst.*, 1894, ii. p. 156).
- Osmond.—*Notes on Hardening of Steel* (*Journal of the Iron and Steel Inst.*, 1896, i. p. 180).
- Howe and Sauveur.—*Further Notes on Hardening* (*Journal of the Iron and Steel Inst.*, 1896, i. p. 170).
- Royston.—*Relation between Carbon and Iron at High Temperatures* (*Journal of the Iron and Steel Inst.*, 1897, i. p. 166).
- Ridsdale.—*Brittleness in Soft Steel* (*Journal of the Iron and Steel Inst.*, 1898, i. p. 220).
- Stead.—*Brittleness in Soft Steel by Annealing* (*Journal of the Iron and Steel Inst.*, 1898, ii. p. 137).
- Le Chatelier.—*Present Condition of the Theories of Hardening* (*Revue Générale des Sciences*, Jan. 15, 1897; *Metallographist*, vol. i., No. 1).
- Ledebur.—*Carbon Condition and Hardening of Steel* (*Stahl und Eisen*, June 1, 1897; *Metallographist*, vol. i., No. 1).

<sup>1</sup> *Proc. Inst. Mech. Eng.*, 1907, p. 245.

- Howe.—*Evidence for the Allotropic Theory* (Eng. and Mining Journal, Dec. 12, 1896; Metallographist, vol. i., No 2).
- A. L. Colby.—*Bibliography of Metallography* (Iron Age, Jan. 27, 1898; Metallographist, vol. i., No. 2, p. 168).
- Sauveur.—*Constitution of Steel* (Technology Quarterly, June 1898; Metallographist, vol. i., No. 3).
- Saniter.—*Allotropic Iron and Carbon* (Journal of the Iron and Steel Inst., i. p. 206).
- Howe.—*Hardening Power of Low Carbon Steel* (Metallographist, vol. i., No. 3).
- Sauveur.—*Relations between Microstructure, Thermal and Mechanical Treatment of Steel* (Journal of the Iron and Steel Inst., 1899, ii. p. 195).
- Osmond.—*Signification of the Critical Points of Iron and Steel* (Metallographist, vol. i., No. 4).
- Roberts-Austen.—*Alloys Research Committee* (5th Report, Inst. Mech. Eng.).
- Jüptner.—*Stahl und Eisen*, 1899.
- Osmond.—*Inferior Limit of  $A_{r_2}$*  (Metallographist, vol. ii., No. 3).
- Sauveur.—*Constitution of Hardened Steel* (Metallographist, vol. ii., No. 4).
- Stansfield.—*Solution Theory of Carburised Iron* (Journal of the Iron and Steel Inst., 1899, ii. p. 169; 1900, ii. p. 317).
- Le Chatelier.—*Changes of State in Iron and Steel* (Comptes Rendus, July 31, 1899).
- Morse.—*Effect of Heat Treatment on .3 per cent. C Steel* (Amer. Inst. Min. Eng., Sept. 1899; Metallographist, vol. iii., No. 2).
- Harbord and Twynam.—*Modern Theories on the Cause of Hardening in Steel*, Journ. West of Scotland Iron and Steel Inst., 1897-8).
- Le Chatelier.—*Phase Law applied to the Consideration of Rocks and Metals* (Comptes Rendus, Jan. 8, 1900; Metallographist, vol. iii., No. 4).
- Roozeboom.—*Iron and Steel from the Point of View of the Phase Doctrine* (Journal of the Iron and Steel Inst., 1900, ii. p. 311).
- Fay and Badlam.—*Effect of Annealing upon the Physical Properties and the Micro-structure of a Low Carbon Steel* (Technology Quarterly, Dec. 1900).
- A. Campion.—*Some Experiments on the Methods of Annealing Steel* (Journ. West of Scotland Iron and Steel Inst., 1901).
- Osmond and Le Chatelier.—*Iron and Steel from the Point of View of the Phase Doctrine* (Bulletin de la Soc. d'Encouragement, Nov. 30, 1900).
- C. H. Ridsdale.—*The Correct Treatment of Steel* (Journal of the Iron and Steel Inst., 1901, ii. p. 52).
- Baron H. von Jüptner.—*Iron and Steel from the Point of View of the Phase Doctrine* (Journal of the Iron and Steel Inst., 1901, i. 229).
- J. O. Arnold and A. MacWilliam.—*Micro-structure of Hardened Steels* (Journal of the Iron and Steel Inst., 1902, i. 120).
- Vanderheyem.—*Heat Treatment of Steel* (Iron Age, 1902, p. 12).
- Bunt.—*Oil Tempering* (Engineering, vol. lxxiii. p. 794).
- A. Campion.—*Heat Treatment of Steel under Conditions of Steelworks Practice* (Journal of the Iron and Steel Inst., 1903, i. p. 378).
- J. E. Stead and A. W. Richards.—*Restoration of Dangerously Crystalline Steel by Heat Treatment* (Journal of the Iron and Steel Inst., 1903, ii. 119).
- J. E. Stead and A. W. Richards.—*Sorbitic Steel Rails* (Journal of the Iron and Steel Inst., 1903, ii. 141).
- W. Campbell.—*Heat Treatment of Steel* (Journal of the Iron and Steel Inst., 1903, ii. 359).
- A. Stansfield.—*Burning and Overheating of Steel* (Journal of the Iron and Steel Inst., 1903, ii. 433).
- H. C. H. Carpenter and B. F. E. Keeling.—*The Range of Solidification and the Critical Ranges of Carbon Iron Alloys* (Journal of the Iron and Steel Inst., 1904, i. 224).

- Roberts-Austen and W. Gowland.—*Alloys Research Committee* (6th Report Inst. Mech. Eng.).
- H. Le Chatelier.—*Composition of Quenching Baths* (Revue de Métallurgie, 1904, pp. 303-304).
- J. O. Arnold and A. MacWilliam.—*The Thermal Transformations of Carbon Steels* (Journal of the Iron and Steel Inst., 1905, ii. p. 27).
- P. Breuil.—*Constitution of Hardened Steels* (Bulletin de la Société de l'Industrie Minérale, vol. vi. pp. 553-683).
- P. Longmuir.—*Hardened Steels* (Journal of the Iron and Steel Inst., 1907, iii. p. 137).
- L. Demozay.—*The Hardening of Steel* (Journal of the Iron and Steel Inst., 1907, iii. p. 144).

**Special Note on Constituents of Steel.**—The Congress of the International Association for Testing Materials have recently (Sept. 1909) adopted a series of definitions of the constituents of steel from which the terms *Troostite* and *Sorbite* were omitted, but in which the constituent which is present in hardened and tempered steels as an intermediate stage between *Martensite* and *Pearlite* is defined under the name *Osmondite*.

## CHAPTER V.

### PYROMETRY.

**Pyrometry.**—This term is applied to the measurement of high temperatures. It is not possible, it is true, to attain as accurate measurements of high temperatures as it is of low ones by the aid of thermometers; nevertheless, very precise determinations have been made, and, as the measurement of high temperatures is of great importance in metallurgy, some attention must be devoted to the principles on which pyrometry is based.

The author has elsewhere pointed out<sup>1</sup> that, notwithstanding the importance attached by early experimenters to the action of heat on metals, they had but little definite information respecting the relative degrees of intensity of heat; and their views were not inadequately expressed in the eighth century by Geber, who stated that great difficulties arose in conducting operations with the aid of heat, because heat cannot be measured, "*sed quoniam non est res ignis, quæ mensuari possit.*"<sup>2</sup> The name of Josiah Wedgwood is always associated with the early attempts to provide a practical method of pyrometry; but, although he wrote a thousand years after Geber, he seems to have merely changed the language of the latter, "heat cannot be measured," into a lament that there were no trustworthy instruments for effecting the measurement of "the higher degrees of heat, from a red heat up to the strongest that vessels made of clay can support."<sup>3</sup> He therefore devised a pyrometer which depended on the contraction that clay experiences when strongly heated. It is not necessary to give a history of pyrometry in this place; the author would merely point out that Wedgwood demonstrated the necessity for the accurate measurement of high temperatures, and that, from his time, the invention of more or less suitable instruments has proceeded rapidly.

<sup>1</sup> Lecture at the Royal Institution. *Nature*, vol. xlv., 1892, p. 534.

<sup>2</sup> From the edition of his *Summa Perfectionis Magisterii*, published in Venice, 1542, p. 28. (Additions have probably been made to Geber's original text.)

<sup>3</sup> *Phil. Trans. Roy. Soc.*, vol. lxxii., 1782, p. 305.



In the long interval between the work of Wedgwood and that of the late Sir William Siemens, such pyrometric appliances as were actually in industrial use depended mainly on what is known as the "method of mixtures,"—that is, upon the employment of a body, the specific heat of which was known, to transfer or carry heat from a furnace, or source of heat, to a measured volume of water, the rise in temperature of which was indicated by an ordinary thermometer. Pyrometers depending on the expansion of metallic strips or rods are also employed; but they may all be set aside with the general statement that, although they are useful in affording rough approximate measurements, they are useless for accurate pyrometry. It may be well to add that a noteworthy advance in thermometry was made a few years ago in Professor Ramsay's laboratory at University College by Messrs Baly and Chorley, who employ the fluid alloy of sodium and potassium, instead of the mercury of the ordinary thermometer; temperatures of 600° Centigrade may thus be measured by making the thermometers of very hard glass.

By introducing nitrogen into the stem of thermometers above the mercury they may be used up to 500°, and it may be added that glass thermometers filled with petrol may be used to measure temperatures as low as - 200° C.

Carl Barus<sup>1</sup> has given the following classification of the principles on which pyrometers have been constructed in an admirable treatise on the measurement of high temperatures:—

- |                               |                                   |
|-------------------------------|-----------------------------------|
| 1. Dilatation of solids—      | 6. Fusion.                        |
| (a) A single solid;           | 7. Ebullition.                    |
| (b) Two solids acting differ- | 8. Specific heat.                 |
| entially.                     | 9. Heat conduction.               |
| 2. Dilatation of liquids.     | 10. Heat radiation.               |
| 3. Dilatation of gases—       | 11. Viscosity—                    |
| (a) Expansion measured in     | (a) of solids;                    |
| volume, manometri-            | (b) of liquids;                   |
| cally;                        | (c) of gases.                     |
| (b) Expansion measured in     | 12. Spectrophotometry and colour. |
| pressures, manometri-         | Rotary polarisation.              |
| cally;                        | 13. Acoustics (wave-length).      |
| (c) Expansion measured in     | 14. Thermo-electrics.             |
| volume, by displace-          | 15. Electrical resistance.        |
| ment.                         | 16. Magnetic moment.              |
| 4. Vapour tension.            | 17. Miscellaneous.                |
| 5. Dissociation.              |                                   |

This classification shows that almost every thermal phenomenon has been utilised for pyrometry. It is especially necessary for the student to know what appliances afford a means of estimating high temperatures with sufficient accuracy for the ordinary purposes of a metallurgical works, and are at the same time

<sup>1</sup> *Bulletin of the United States Geological Survey*, No. 54, Washington, 1889. This contains an exhaustive bibliography of pyrometry.

sufficiently durable to withstand rough usage. For delicate investigations there are several instruments that can safely be adopted. These will be described subsequently.

Mr R. S. Whipple, who has contributed much to the progress of technical pyrometry, has given the following very useful table of types of thermometers in general use.<sup>1</sup>

#### TYPES OF THERMOMETERS IN GENERAL USE.

	Principle.	Type.	Range in Degrees C.
Expansion . . . . .	Those depending on the change in volume or length of a body with temperature.	Gas . . . . .	0 to 1,000
		Mercury, Jena glass, and nitrogen . . . . .	- 40 " 500
		Glass and spirit or petrol . . . . .	- 200 " + 40
		Unequal expansion of metal rods . . . . .	0 " 500
		Contraction of porcelain . . . . .	0 " 1,800
Transpiration and Viscosity . . . . .	Those depending on the flow of gases through capillary tubes or small apertures.	The Uehling . . . . .	0 to 1,600
Thermo-electric . . . . .	Those depending on the E.M.F. developed by the difference in temperature of two similar thermo-electric junctions opposed to one another.	Galvanometric . . . . .	0 to 1,600
		Potentiometric . . . . .	0 " 1,600
Electric Resistance . . . . .	Those utilising the increase in electric resistance of a wire with temperature.	Direct reading on indicator or bridge and galvanometer . . . . .	0 to 1,200
Radiation . . . . .	Those depending on the heat radiated by hot bodies.	Thermo-couple in focus of mirror . . . . .	0 to 10,000
		Bolometer . . . . .	0 " 10,000
Optical . . . . .	Those utilising the change in the brightness or in the wave-length of the light emitted by an incandescent body.	Photometric comparison . . . . .	0 to 2,000
		Incandescent filament in telescope . . . . .	0 " 2,000
		Nicol with quartz and analyser . . . . .	0 " 2,000
Calorimetric . . . . .	Those depending on the specific heat of a body raised to a high temperature.	Copper or platinum ball with water vessel . . . . .	0 to 1,500
Fusion . . . . .	Those depending on the unequal fusibility of various metals or earthenware blocks of varied composition.	Alloys, etc., of various fusibilities . . . . .	0 to 1,980

<sup>1</sup> *Proc. Western Soc. of Engineers, Chicago, vol. xii., No. 2.*

The simplest methods are undoubtedly grouped in class 6 of Barus' "fusion." For instance, the insertion of a fragment of metal of known melting-point in the locality whose temperature is to be tested will often afford at once the required information. Thus the temperature of the hot blast may be capable of melting a rod of lead (melting-point  $327^{\circ}$ ), though it may fail to melt a similar rod of zinc (melting-point  $419^{\circ}$ ). A strip of pure silver will just melt at a temperature at which zinc boils, and this has been accurately determined as being  $961^{\circ}$ ; and it follows, therefore, that a temperature which will just melt pure silver is somewhere near  $960^{\circ}$ .

This method of "fusion" has been greatly improved by Dr H. Seger of Berlin, who has devised and manufactured a series of cones which are known as "Seger Cones," and which consist of truncated pyramidal-shaped bodies, composed of a graduated mixture of aluminium silicates, which soften and fuse at definite temperatures, and by the aid of which it is possible to determine the approximate temperatures of furnaces and of heated spaces. The following table gives the numbers of the series used in practice, together with the approximate temperature at which they fuse.<sup>1</sup>

No.	Temp. in Degrees C.	No.	Temp. in Degrees C.	No.	Temp. in Degrees C
022	590	03	1090	17	1470
021	620	02	1110	18	1490
020	650	01	1130	19	1510
019	680	1	1150	20	1530
018	710	2	1170	21	1550
017	740	3	1190	22	1570
016	770	4	1210	23	1590
015	800	5	1230	24	1610
014	830	6	1250	25	1630
013	860	7	1270	26	1650
012	890	8	1290	27	1670
011	920	9	1310	28	1690
010	950	10	1330	29	1710
09	970	11	1350	30	1730
08	990	12	1370	31	1750
07	1010	13	1390	32	1770
06	1030	14	1410	33	1790
05	1050	15	1430	34	1810
04	1070	16	1450	35	1830
				36	1850

It must be remembered that the above figures are only an approximation to the true temperatures, but this approximation is sufficiently accurate for numerous industries or operations. By

<sup>1</sup> *Journ. Iron. and Steel Inst.*, 1904, No. 1, p. 117.

standardising a number of intermediate cones by means of the thermo-electric pyrometer, and by definitely determining the softening points of the most readily fusible and of the most refractory cones respectively, and adjusting the remainder by interpolation, a series is obtained which, assuming the incremental variations to be correctly expressible as constants, will at least furnish a useful indication of temperature.

In practice, a number of cones are placed in the furnace, ranging over perhaps 8 or 10 numbers in sequence. At the end of the experiment the cones will be found to be variously affected, some having completely collapsed, while others are hardly altered.

The temperature is taken to be that at which a particular cone in the series appears to present a mean degree of fusing.

The cones are made up of mixtures in various proportions of quartz, kaolin, white marble, and felspar, the raw materials used for glazes at the Royal Berlin Factory.

Many appliances, notably the Siemens Water Pyrometer, may be purchased, the action of which depends upon the method of mixtures (No. 8 in Barus' scheme). This is shown in cross section in fig. 63, and consists of a cylindrical copper vessel provided with a handle and containing a smaller copper vessel. An air-space *a* separates the two vessels, and a layer of felt surrounds the inner one in order to retard the exchange of temperature with the surroundings. The capacity of the inner vessel is a little over one pint.

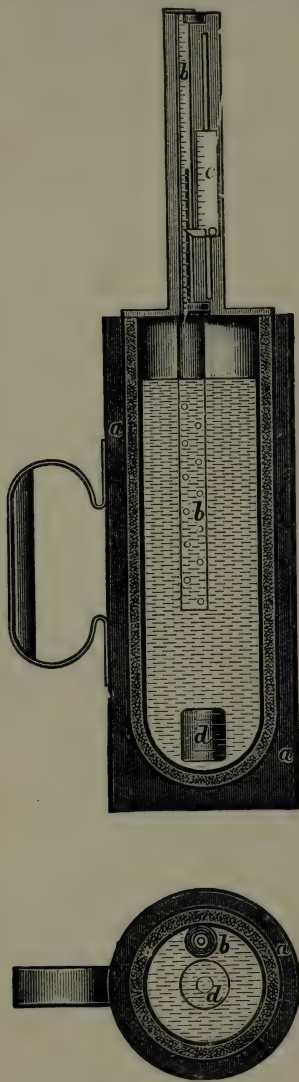


FIG. 63.

A mercury thermometer *b* is fixed close to the wall of the inner vessel, its lower part being protected by a perforated brass tube, whilst the upper



part projects above the vessel, and is divided as usual on the stem into degrees.

At the side of the thermometer there is a small brass scale *c*, which slides up and down, on which the high temperatures are marked; on a level with the zero division of the brass scale a small pointer is fixed, which traverses the scale of the thermometer. Small cylinders *d*, of either nickel, copper, iron, or platinum, which are so adjusted that their heat capacity at ordinary temperature is equal to one-fiftieth of that of the copper vessel containing one pint of water, are used. As, however, the specific heat of metals increases with the temperature, allowance is made on the brass sliding scales, which are divided according to the metal of which the cylinders are composed.

The water pyrometer is used in the following manner:—

Exactly one pint of clean water is poured into the copper vessel, and the pyrometer is left for a few minutes to allow the thermometer to attain the temperature of the water. The brass scale *c* is then set with its pointer opposite the temperature of the water, as shown by the thermometer. Meanwhile one of the metal cylinders has been exposed to the high temperature which is to be measured, and, after allowing sufficient time for it to acquire that temperature, it is rapidly withdrawn and carefully dropped into the pyrometer vessel. The temperature of the water then rises, and when the mercury of the thermometer has become stationary, the degrees are read off, as well as those on the brass scale opposite the top of the mercury.

The sum of these two values gives the temperature of the heated space in which the metal cylinder has been placed. With cylinders of iron or copper, temperatures up to 1000° C. or 1800° F. can be measured, and with cylinders of platinum temperatures up to 1500° C. or 2700° F.

For ordinary furnace work either copper or wrought-iron cylinders may be used. Iron possesses a higher melting-point and has less tendency to scale than copper, but the latter is affected much less by the action of the furnace gases. Nickel may be used up to 1400° C., and possesses advantages in freedom from scaling and from attack by the gases.

The weight to which the cylinders are adjusted are as follows:—

Copper . . . . .	137 grammes.
Wrought iron . . . . .	112 „
Nickel . . . . .	117 „
Platinum . . . . .	402·6 „

In the case of copper cylinders, which lose weight by scaling, a certain correction has to be added to the figures to allow for this loss, after they have been in use some time.

For rapid determinations of high temperatures in works the

pyrometer of Carnelly and Burton<sup>1</sup> (class 9 of Barus) may be used. It is cheap and does not readily get out of order; moreover, when once placed in position, it requires little or no manipulation except the reading off of a couple of thermometers and a reference to a table. The principle on which it is based is as follows:—If a current of water of known temperature be allowed to flow at a constant rate through a coiled metallic tube placed in the space the temperature of which is required, then the increase in the temperature of the outflowing water will be greater the higher the temperature of the space.

A new era in the measurement of heat began with the work of Sir William Siemens. He showed<sup>2</sup> that electrical resistance might be used practically in pyrometry. Fig. 64 gives a general

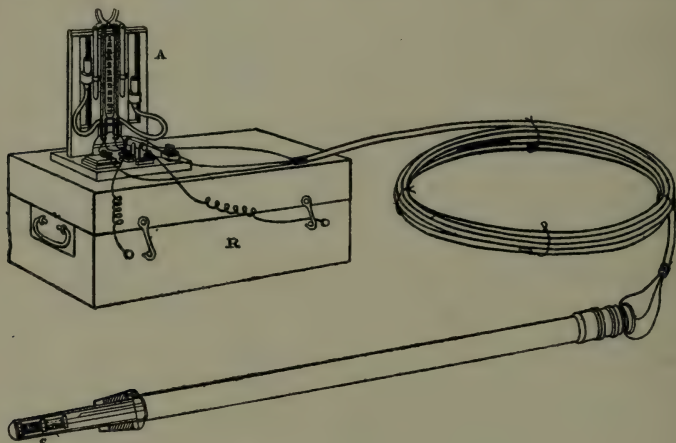


FIG. 64.

view of his apparatus, and its nature is explained by the accompanying diagram, fig. 65. A divided current passes from the battery B to a platinum wire C (coiled round a clay cylinder), and to a resistance coil R. At the ordinary temperature, the resistance of the platinum coil is balanced by the standard resistance R, and an equal current will flow through each. If, however, the platinum coil C be heated, its resistance will be increased, and this increase of resistance can be measured in various ways. Siemens adopted for use in works a small voltmeter, shown at A, fig. 64; the current sent through the platinum coil *c* was of sufficient strength to decompose acidulated water, and the difference in the amount of water decomposed by that portion of the current which passed through the heated

<sup>1</sup> *Journ. Chem. Soc.*, vol. xlv. (1884), p. 237.

<sup>2</sup> Collected papers.

coil, as compared with that decomposed by the current transmitted through the standard resistance at R, fig. 65, gave, on reference to a table, the temperature to be determined. For many years this electrical-resistance pyrometer was the only appliance, believed to be trustworthy, which could be placed in the hands of artificers. Its usefulness was widely recognised, and a Committee of the British Association was appointed to report upon it. The result of the inquiry<sup>1</sup> rather tended to shake confidence in the instrument, as it was shown that it was liable to changes of zero. Prof. Callendar<sup>2</sup> has, however, done much to prove that, with certain precautions, the method may be rendered very trustworthy. He winds the platinum wire on a plate of mica, excludes reducing gases, as the Committee suggested, by enclosing the coil in a tube of doubly-glazed porcelain, and uses a zero method for measuring the resistances with the galvanometer. Fig. 66 represents, somewhat diagrammatically, the arrangement of the apparatus.<sup>3</sup>

A B, B C are equal resistances, forming the arms of the balance. The battery is connected at A and C, and one terminal of the galvanometer G at B. D E represents a set of resistance coils, which, together with the resistances A B and B C, may be supplied by an ordinary box of coils of the "post-office" pattern. F K represents a straight bridge-wire, with a divided scale attached. The other terminal of the galvanometer is connected to the contact-piece H, which slides along this wire. The leads A M, K N from the

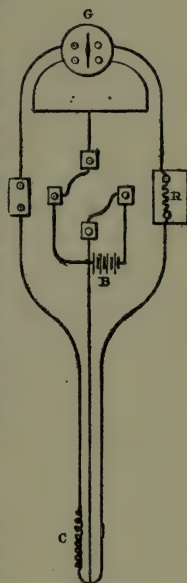


FIG. 65.

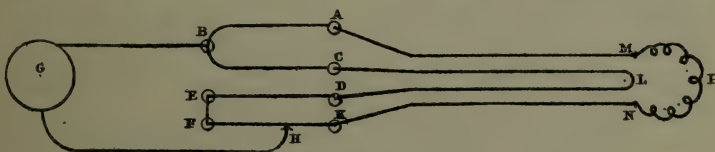


FIG. 66.

pyrometer coil P are connected to A and K; and the compensating leads C L, L D, the resistance of which is equal to A M, K N, are connected to C and D. These four leads may be of any convenient length; they are symmetrically arranged, so that corresponding parts are always at the same

<sup>1</sup> *British Association Report*, 1874, p. 242.

<sup>2</sup> *Phil. Trans. Roy. Soc.*, vol. clxxviii., 1887, p. 161.

<sup>3</sup> *Phil. Magazine*, vol. xxxii., 1891, p. 104, and vol. xxxiii., 1892, p. 220.

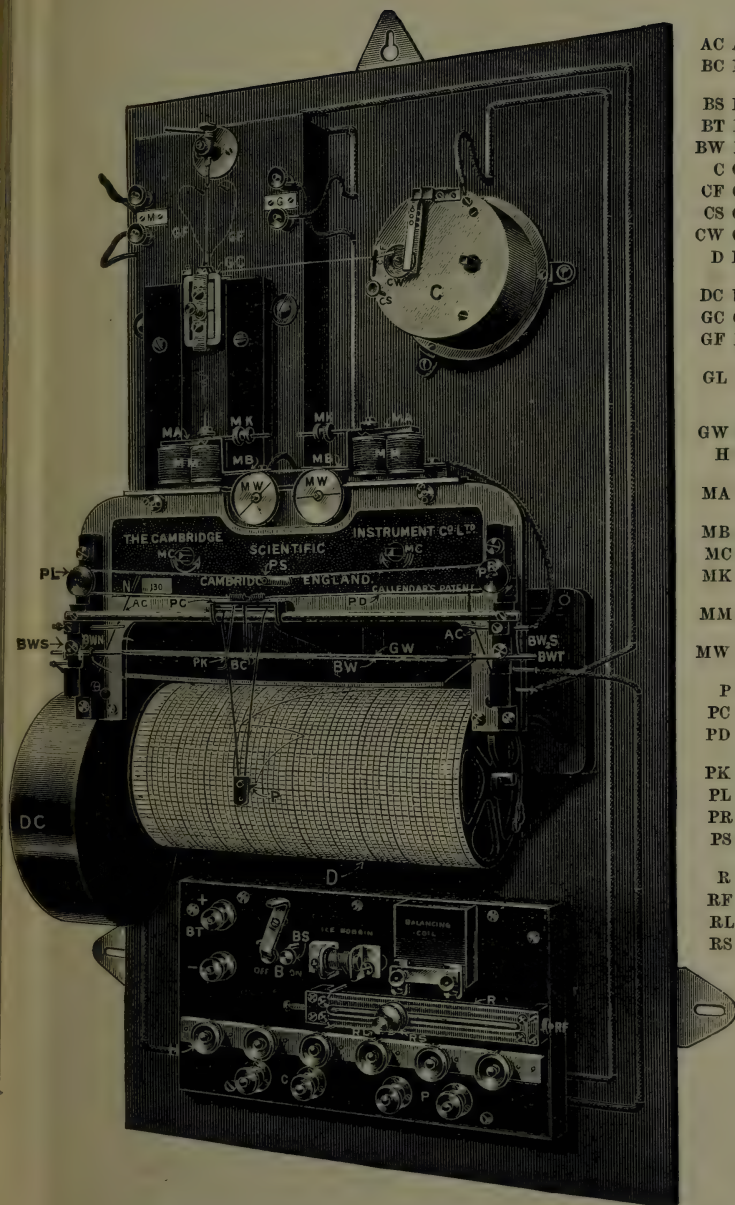


temperature. When the balance is found by inserting suitable resistances in the arm D E, and sliding the contact-piece H, it is plain that, since the resistances A B, B C are equal, the resistance of the pyrometer and its leads, together with that of the length H K of the bridge-wire, will be equal to the remaining portion F H of the bridge-wire, together with the coils D E, and the compensation C L D. Thus the changes of the resistance of the pyrometer leads A M, K N are compensated by the equal changes in the leads C L, L D, and the resistance of the pyrometer coil itself is directly given by the sum of the coils D E and the reading of the bridge-wire. The resistance of a centimetre of the bridge-wire F K is made to correspond to such an increase of the resistance of the pyrometer coil P as is produced by a rise of  $1^{\circ}$  C. The contact-key H slides along this wire, and the galvanometer can easily be made sensitive to one-hundredth of a centimetre of this bridge-wire, so that one-tenth of a centimetre, which corresponds to one-tenth of a degree, can, of course, be measured with certainty.

For reading temperatures directly by means of a resistance thermometer, the Whipple Temperature Indicator is often used. It consists of a Wheatstone Bridge, one arm of which is a long bridge-wire in the form of a helix on an ebonite drum. A contact-maker mounted on the inside of a drum can be rotated over this wire. A scale, divided into degrees, is fixed on the outer surface of the drum. The four terminals of the resistance thermometer are connected by means of leads to the indicator, the resistance coil of the thermometer thus forming one arm of the bridge. By turning the handle, the contact-maker is moved along the bridge-wire until sufficient resistance is introduced to balance the resistance of the thermometer. The galvanometer needle shows when this electrical balance has been obtained. A pointer shows the temperature on the scale previously mentioned.

For recording temperatures by means of an electric resistance pyrometer, a Callendar Recorder is used. This instrument, shown in fig. 67, and diagrammatically in fig. 68, consists of a self-adjusting recording Wheatstone Bridge or Potentiometer, in which the movements of the slider along the bridge-wire is automatically effected by relays worked by the current passing through the galvanometer between the bridge arms. According as the moving coil of this galvanometer is deflected in one direction or the other, a relay circuit is connected through one or the other of two electro-magnets. Each of these magnets is mounted on a clock, the movement of which is prevented by a brake. When a current passes through a magnet, this brake is lifted, allowing the clock-work to revolve. These clocks are connected by differential gearing with a recording pen, which is pulled in one direction or the other when the brake is lifted from the corresponding clock. The bridge slide moves with the pen and tends to restore balance.





- AC Automatic cut-outs.
- BC Bridge contact springs.
- BS Battery switch.
- BT Battery terminals.
- BW Bridge wire.
- C Contact clock.
- CF Contact fork.
- CS Contact clock starter.
- CW Contact wheel.
- D Drum carrying record sheet.
- DC Drum driving clock.
- GC Galvanometer coil.
- GF Fine wire connections to contact fork.
- GL Lifter and clamping screw for galvanometer coil.
- GW Galvanometer wire.
- H Milled heads to zero coils.
- MA Motor magnet armatures.
- MB Motor clock brakes.
- MC Motor clocks.
- MK Adjusting weights or motor brakes.
- MM Motor release magnets.
- MW Motor clock brake wheels.
- P Pen.
- PC Pen carriage.
- PD Pen carriage driving cord.
- PK Pen lifter spring.
- PL Left-h. cord pulley.
- PR Right-h. cord pulley.
- PS Pen carriage driving screw.
- R Rheostat.
- RF Rheo. fine adj.
- RL Rheo. locking screw.
- RS Rheo. contact screw.

FIG. 67.—Callendar Recorder, Laboratory Pattern, front removed.

In the pattern of recorder specially designed for laboratory use a number of resistance coils are provided, which are put in circuit by unscrewing the milled brass heads H, fig. 67. With a standard thermometer these coils have the effect of raising the zero of the record to the values 50°, 100°, 200°, 300°, 400°, and 1000°, thus giving a more or less open scale, as may be desired.

Measuring the increased resistance of a heated conductor is not the only way in which electricity has been made serviceable in the measurement of high temperatures. It has long been known that if a junction of two metals be heated, the electrical equilibrium of the system is disturbed, and the measurement of the difference of potential produced affords a means of estimating the temperature of the junction. The use of such thermo-junctions appears to have been suggested by A. C. Becquerel in 1826, and adopted by Pouillet<sup>1</sup> ten years later. Unfortunately, the metals composing the thermo-junctions were badly chosen, and their use was consequently greatly retarded until, in 1887, Professor H. Le Chatelier<sup>2</sup> advocated the use of platinum, in conjunction with platinum alloyed with 10 per cent. of rhodium. The author first adopted this couple in 1889, and afterwards constantly used it, in conjunction with a photographic recorder, devised for the purposes of an investigation which was entrusted to him by the Institution of Mechanical Engineers. C. Barus has shown that the indications afforded by thermo-junctions are trustworthy at very high temperatures, and he has enabled great confidence to be placed in the platinum platinum-iridium thermo-junction originally suggested by Tait. In its latest form the instrument consists of two wires, one of the metal and the other of the alloy mentioned above, simply twisted at their ends or "autogène," soldered by means of the oxyhydrogen flame, which method is much to be preferred, and connected with a dead-beat galvanometer of about 200 ohms resistance. The suspended coil galvanometer, particularly the later types of this instrument, is admirably adapted for use with this thermo-couple.

The deflections of the galvanometer may be converted into thermometric degrees by Tait's empirical formula,

$$E = A(T_1 - T_0) + B(T_1^2 - T_0^2),$$

in which  $E$  is the electro-motive force in terms of the absolute temperature  $T_1$  and  $T_0$  of the two elements of the couple. It is only necessary to introduce into this formula the values of  $E$  corresponding to two fixed points, in order to determine the coefficients  $A$  and  $B$ , and to construct a table of ordinary temperatures corresponding to each millimetre of the scale. Le Chatelier, however, showed that the second term of the equation

<sup>1</sup> *Comptes Rendus*, vol. iii. (1836), p. 782.

<sup>2</sup> *Bull. Soc. Chim. Paris*, vol. xlvii. (1887), p. 2; *Journ. de Physique*, vol. vi. (1887), p. 23.

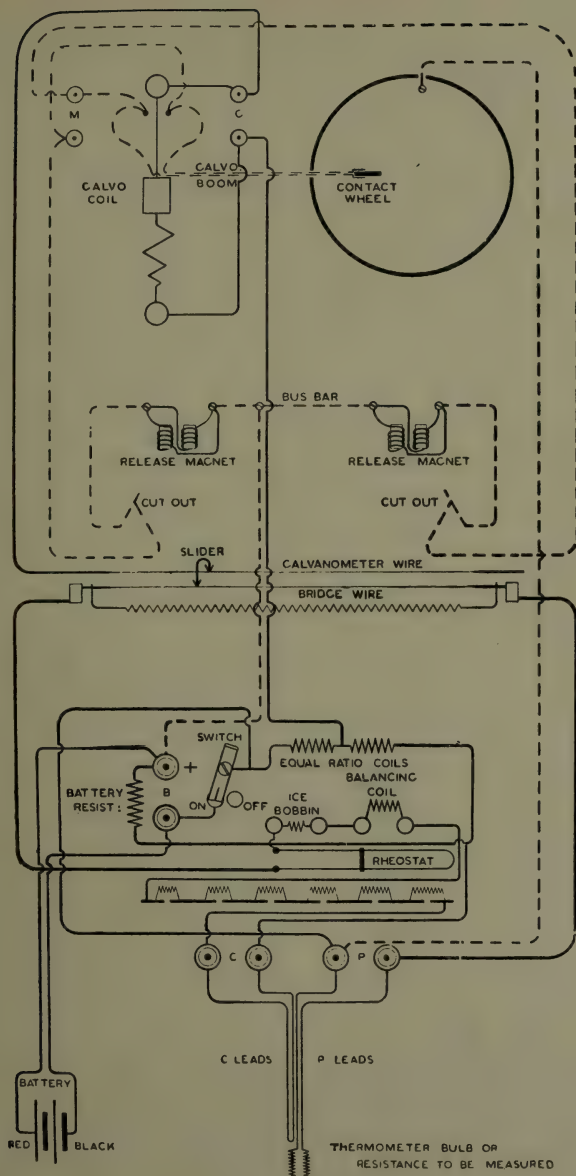


FIG. 68.

C Terminals for "C" leads, P Terminals for "P" leads.

(a parabola) ceased to be of importance with the platinum platinum-rhodium couple for high temperatures, and that between 300° and 1200° the equation becomes approximately that of a straight line,

$$E = a + bt,$$

in which  $E$  is the electro-motive force,  $t$  the observed temperature, and  $a$  and  $b$  numerical coefficients.<sup>1</sup>

One important feature is the small space occupied by the thermo-junction, which may be suitably protected, and inserted into the midst of a very small mass of metal. The pyrometer is calibrated by exposing the thermo-junction to certain known temperatures, such as the solidifying points of salts or metals. There is no difficulty in recognising the melting or the solidifying point; for, as the mass passes from the solid to the fluid state, the temperature remains constant for a brief period, the duration of which depends on the amount of material operated upon, and its latent heat of fusion; the result being that the spot of light from the galvanometer will be arrested, and the position on the scale, at which it stops, marks the temperature to be determined. Increased sensitiveness in this method of detecting and recording molecular changes has been obtained<sup>2</sup> by arranging that a portion of the current of the thermo-couple is balanced by an opposing electro-motive force from a Clark's cell.

The electro-motive force produced by heating the thermo-junction to any given temperature is measured by the movement of the spot of light on the scale, and, as has been above indicated, the scale is calibrated by heating the thermo-junction in contact with substances of known melting-points.

The following list gives a sufficient number of such fixed points, which have been established by concurrent evidence of various kinds:—

100° Centigrade	.	.	.	Boiling-point of water.
232	"	.	.	Melting-point of tin.
327	"	.	.	" " lead.
419	"	.	.	" " zinc.
445	"	.	.	Boiling-point of sulphur.
657	"	.	.	Melting-point of aluminium.
860	"	.	.	" " sodium sulphate.
1084	"	.	.	" " copper.

They rest mainly, however, on determinations made with the air thermometer.

Some years ago Carnelly<sup>3</sup> determined the melting-points of certain substances by the method of mixtures, and used them,

<sup>1</sup> For a further development of this formula, see Osmond, *Transformations du Fer et du Carbone* (Paris, 1888), p. 16.

<sup>2</sup> Alloys Research Committee, *Inst. Mech. Eng.*, 4th Report.

<sup>3</sup> *Journ. Chem. Soc.*, vol. xxxiii. (1878), pp. 273, 281; vol. xlv. (1884), p. 237.



when enclosed in capillary tubes of glass, to ascertain at what temperatures substances of unknown melting-points actually fuse. Le Chatelier<sup>1</sup> has since tested, with the aid of his thermo-couple, the accuracy of Carnelly's experiments, and has obtained in many cases very concordant results, as is shown in the following table:—

TABLE OF MELTING-POINTS.

	Le Chatelier.	Carnelly.
Potassium chloride . .	740°	734°
Sodium „ . .	775	772
Calcium „ . .	755	719
Barium „ . .	847	772
Tin (SnCl <sub>2</sub> ) „ . .	840	812
Sodium carbonate . .	810	814
Barium „ . .	795	
Potassium „ . .	885	834
Sodium sulphate . .	867	861
Barium nitrate . .	592	
Potassium sulphate . .	1015	
„ bichromate . .	975	
Sodium phosphate . .	957	
Potassium chlorate . .	370	359
Cuprous sulphide . .	1100	
Pure white pig-iron . .	1135	
Grey pig-iron . .	1240	
Grey forge pig-iron . .	1220	

The details of the method to be adopted in using a *thermo-electric pyrometer* will vary according to the nature of the investigation to be undertaken.

In the first place, the choice of couple will depend on the range of temperature required to be covered during the observation, and as a general rule it may be taken that copper-constantan couples may be used for temperatures up to 500° C., giving a very open scale; platinum-platinum-iridium couples may be used for temperatures up to 1400° C., as these give a more open scale than platinum-rhodium couples, and finally platinum-platinum-rhodium couples should be used if it is required to go up to 1600° C.

When accurate measurements are required, it is necessary to introduce a cold-junction, that is to say, arrangements are made to keep the junction of the pyrometer wires and the galvanometer leads at a constant or known temperature; for this purpose they are enclosed in a bottle containing cold water, and the temperature noted by means of a thermometer; or kept in an ice box, temperature 0°, or in a steam box, temperature 100°.

<sup>1</sup> *Bull. Soc. Chim. Paris*, vol. xlvii. (1887), p. 300.

For this book three types of investigation may be considered, viz. (1) The simple melting-points of alloys; (2) A continuous record of furnace temperatures; and (3) The thermal changes which take place during the cooling of a piece of steel.

1. For determining the freezing-points of alloys, a couple consisting of platinum and platinum-iridium, containing 10 per cent. iridium, may be used. The wires composing the couple are insulated their whole length by threading them through double-drilled fireclay tubes, and the couple end is placed in a clay, silica, or hard glass tube closed at one end. Care must be taken that the wires do not touch except at the junction. The free ends of the pyrometer wires are connected with copper leads which pass to the galvanometer, including in the circuit a suitable resistance to get the correct range of movement on the scale for the temperatures required. As already mentioned,

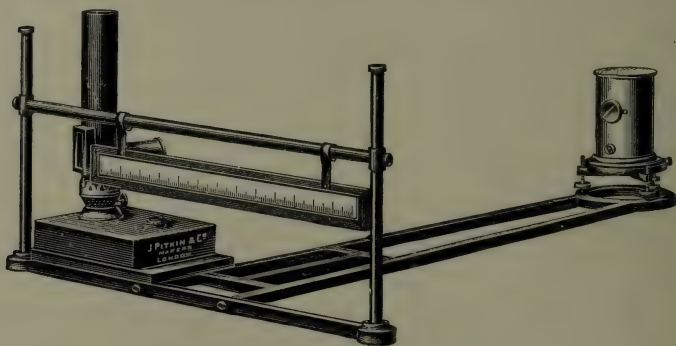


FIG. 69.

the connection between the platinum wires and the copper leads should be kept at a constant temperature.

Fig. 69 shows a suitable stand, including galvanometer, lamp, and scale, for taking the readings, made by Messrs Pitkin.

The couple is first calibrated by taking several readings from metals of known freezing-points, and these are plotted into a curve, having as co-ordinates scale readings and temperatures. Then this curve is used for interpreting the result of scale readings obtained from materials of unknown freezing-points.

There are several kinds of curves obtained by this method, the most important being *time-temperature* and *inverse-rate* curves. For the former, the position of the ray of light is taken at regular intervals of time and plotted with the time, and for the latter the time required for the ray of light to pass regular intervals or divisions on the scale is taken and plotted with the temperature.

2. For taking a continuous record of furnace temperatures,

etc., either a photographic or autographic method is most suitable.

The photographic recorder which was devised by the author<sup>1</sup> may be described as consisting of two mahogany cases, fig. 70, impervious to light, the larger of which (A) contains a Holden-d'Arsonval dead-beat galvanometer, with a suitable arrangement of lenses and mirrors. The other case (B) contains a drum which is made to revolve by clockwork once in 24, 12, or 6 hours. A ray of light, either from a gas jet or from an electric lamp, is thrown, by means of a mirror placed at an angle of  $45^\circ$ , on to the mirror of the galvanometer, and is projected thence to the surface of the drum, acting photographically on the sensitised paper. The galvanometer is connected by copper leads to a

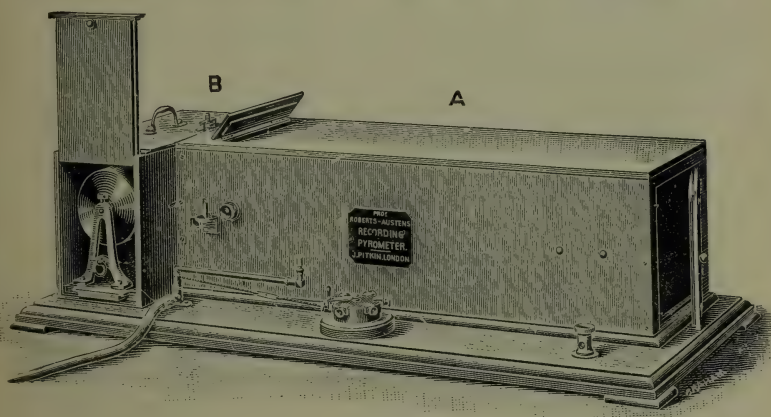


FIG. 70.

thermo-junction inserted in the space or object, the temperature of which it is desired to record. Another form of this apparatus (also made by Messrs Pitkin) is often used in which the revolving drum is replaced by a dark slide containing a photographic plate, and which is made to move vertically by clockwork. It must be understood that this form of instrument can equally well be used for recording freezing-points of alloys and thermal changes of metals: the movement of the ray of light varying with the temperature, and the position of the drum varying with time, gives a record which can readily be interpreted.

As an example of the autographic method of recording temperatures, mention may be made of the Patent Thread Recorder of the Cambridge Scientific Instrument Co., of which a

<sup>1</sup> *Journ. Iron and Steel Inst.*, ii., 1892, 33.



general view is shown in fig. 71, and a diagrammatic view of the essential parts is shown in fig. 72.

The galvanometer boom A turning about the axis B (see fig. 72) is depressed every minute or half-minute as desired on to an inked thread G, which is forced against the paper, leaving a small ink mark behind on the paper C. The ink on the thread is renewed by means of a simple winding mechanism. This method of recording gives rectangular co-ordinates, and entirely prevents the blotting or smudging of the record. The instrument can be made extremely sensitive.

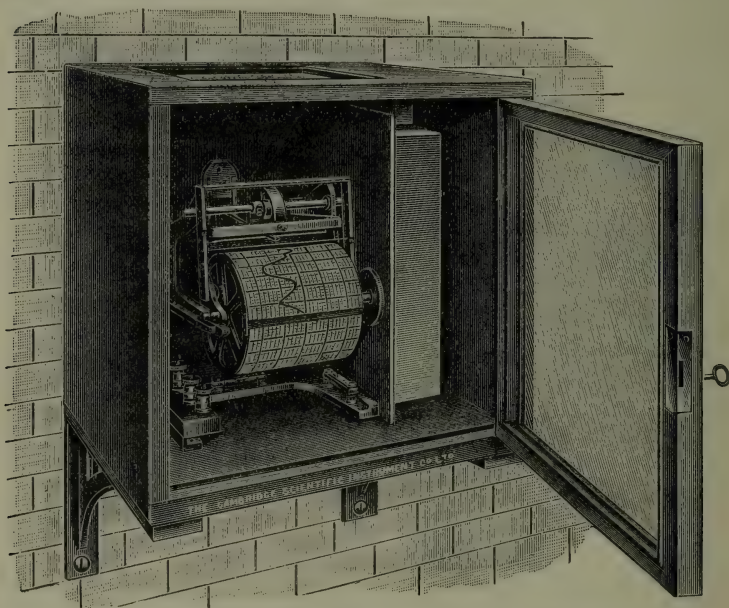


FIG. 71.—Patent Thread Recorder for recording temperatures.

The clockwork mechanism can be made to depress two or more galvanometer booms simultaneously, the various galvanometers being connected to different thermometers. The records obtained are entirely independent of each other, and the thermometers may be working over widely different ranges. If by any mishap one galvanometer or thermometer is damaged, the others are unaffected.

A scale for reading temperatures directly is fixed on the face of the chopper bar D, fig. 72.

The wires of the couple for furnace work are also threaded through double-drilled fire-clay tubes which serve to insulate them, and the whole is inserted in a covering sheath of gas or steam



barrel, the junction end of which is closed by a thin iron disc welded securely into the end. To the open end of the sheathing is fixed a head of cast metal, bored and tapped to fit the iron sheathing.

The cover of this head is made of ebonite, and carries the two terminals to which the wires of the couple are connected, and also the galvanometer leads.

3. For examining the thermal changes that take place during the cooling down of a piece of steel, which is a very important

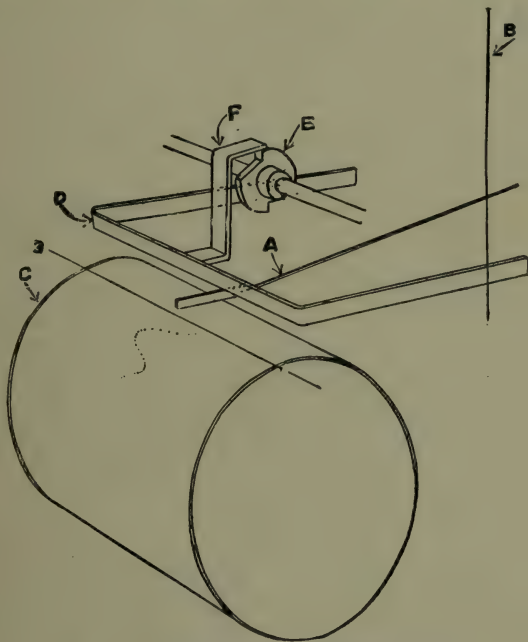


FIG. 72.—Essential parts of Thread Recorder.

matter, as by this means the correct temperature for subsequent thermal and mechanical treatment is ascertained, the differential method is used. This method was devised for use for the Alloys Research Committee<sup>1</sup> work, and has since proved of very great value in determining small thermal changes during the cooling down of metals and alloys.

The method consists essentially in eliminating the general cooling effect during the observation, and noting any differences in temperature of the metal under examination and another metal of similar thermal capacity, but having no critical changes in the

<sup>1</sup> Alloys Research Committee, *Inst. Mech. Eng.*, 5th Report.

range of temperature used during the experiment. For this second metal a piece of nickel steel or platinum is generally used. For these observations two galvanometers are required, one connected with a simple thermo-couple in the usual way to indicate the temperatures, the second galvanometer being connected with a compound couple which only indicates any change of temperature in the two metals used. As these two metals are kept at the same temperature, the ray of light from the second galvanometer will only move when heat is given out or absorbed by critical changes taking place in the metal under examination. Arrangements can be made in the photographic

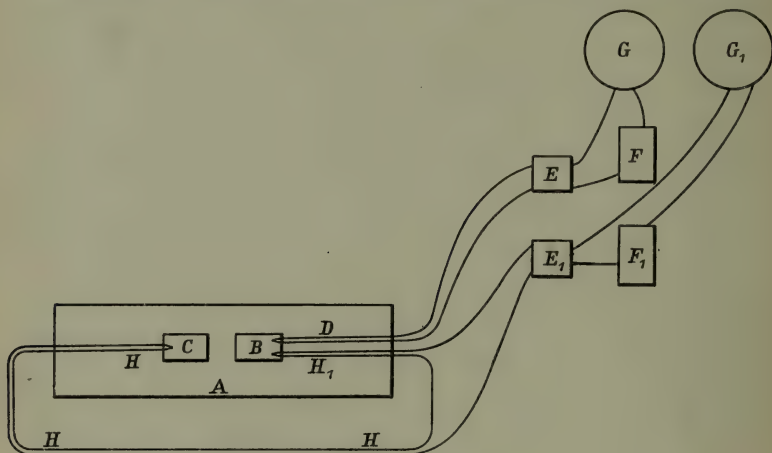


FIG. 73.

- |   |   |
|---|---|
| A Electric furnace.                     | E E <sub>1</sub> Cold-junctions.          |
| B Steel under examination.              | F F <sub>1</sub> Resistance boxes.        |
| C Neutral metal; Ni-steel, or platinum. | G Galvanometer for temperature.           |
| D Thermo-couple for temperature.        | H H <sub>1</sub> Compound thermo-couple.  |
|   | G <sub>1</sub> Differential galvanometer. |

recorder to record the movements of the two galvanometers at the same time, or the readings may be obtained by lamp and scale arrangements.

In any case a curve can be obtained having as co-ordinates actual temperature and differences of temperature between the two metals, that is, heat given out, due to critical changes.

Fig. 73 is a diagram indicating the connections necessary for obtaining differential curves. A is a tube furnace containing an unglazed porcelain tube about 16 inches long and 1 inch in diameter, heated electrically by means of a coil of nickel wire or platinum foil carrying about 20 amperes. B is a cylinder of the steel under examination; it is bored with two holes, one for the

simple thermo-couple D which is connected through the cold-junction E and resistance box F to the galvanometer G, which records the temperature of the steel during heating or cooling. C is a cylinder of nickel steel, having no critical points at the temperatures used, or a cylinder of platinum bored with one hole and containing a thermo-couple H, one wire of which, say the platinum, passes through the cold-junction  $E_1$  and the resistance box  $F_1$  to the differential galvanometer  $G_1$ , the other wire, say the platinum-iridium, passes to  $H_1$ , where it forms with another platinum wire a second thermo-couple, which is placed in the second hole in the steel under examination; this platinum wire now passes through the cold-junction box  $E_1$  to galvanometer  $G_1$ , thus completing the circuit. It will be seen that the thermal changes indicated by this galvanometer will be the algebraic sums of those of the metal B under examination and the neutral metal C.

For really accurate measurements in scientific research, the modification of the air thermometer devised by Deville and Troost may safely be adopted. With regard to it, modifications of the air thermometer in which glass bulbs were replaced by metal were adopted by Prinsep and others early in the last century. The great advance Deville and Troost made was the substitution of bulbs of porcelain for those of metal. The following is an outline of their experimental method:—

Their apparatus consists of a globular flask of Bayeux porcelain of 280 or 300 cubic centimetres capacity, with a neck 11 centimetres long and 4 millimetres in internal diameter. A quantity of iodine is put into the flask, and the neck is nearly closed by a small plug of porcelain, which lies loosely in the opening. When the flask is now exposed to a high temperature, the iodine is vaporised, and the greater part escapes by the neck, driving out at the same time nearly the whole of the air. After the flask has been exposed for about twenty minutes to the temperature that is to be measured, the flame of an oxyhydrogen blowpipe is allowed to play for an instant on the porcelain plug lying in the neck; the plug is thus melted, and closes the flask hermetically. When cold the flask is cleaned and carefully weighed; the end of the neck is broken under boiled water or mercury, and the flask is weighed together with the water or mercury which enters; it is then completely filled with water or mercury and weighed again; lastly, the flask is weighed when empty. From the weights thus obtained it is easy to calculate the capacity of the flask and the volume of the residual air, that is, air which has not been expelled by the iodine vapour. The first weighing gives directly the excess of weight of the flask, and iodine vapour over that of the empty flask. The

observations which require to be made in each experiment are the following:—

Temperature of the balance . . . . .	$t^{\circ}$
Pressure of the atmosphere . . . . .	$h$ millimetres
Excess of weight of sealed flask and iodine vapour at end of experiment over that of the empty flask . . . . .	$i$ grms.
Capacity of flask . . . . .	$v$ cubic centimetres
Residual air . . . . .	$a$ „ „

In order to be able to calculate the exact temperature at which the flask was sealed the following constants are necessary:—

Weight of 1 c.c. air at $0^{\circ}$ and 760 mm. pressure	= 0.001293 grm.
Density of iodine vapour referred to air as unity	= 8.716
Coefficient of expansion of air for $1^{\circ}$ C. . . . .	= 0.00366
Coefficient of cubical expansion of the porcelain for $1^{\circ}$ C. . . . .	= 0.0000108

The required temperature may then be calculated in the following manner:—

Let  $I_w = \left( \frac{(v-a)0.001293}{(1+0.00366\ i)} \frac{h}{760} + i \right)$  be the total weight of iodine vapour contained in the flask at the moment of sealing; then

$$\frac{I_w}{0.001293 \times 8.716} \frac{(1+0.00366\ T) 760}{h} = I_v$$

will be the volume of the vapour at the same moment; but

$$I_v + \frac{a(1+0.00366\ T) 760}{(1+0.00366\ t) h} = v(1+0.0000108\ T),$$

and from this equation, in which  $T$ , the temperature required, is the only unknown quantity, its value is easily found.

Owing to the belief that the molecule of iodine undergoes dissociation at high temperatures, this method has been modified, atmospheric air being used in place of iodine.

Barus has devised a form of appliance which he considers to be superior to that used by Deville for determining the boiling-points of metals. As shown in fig. 74, it consists of a glazed tube of porcelain  $d$ , passed through a hole in the base of a crucible  $a$ . The zinc or other metal whose boiling-point is to be determined is shown at  $k$ . In this case a thermo-couple is used as a pyrometer, and it is inserted into the porcelain tube  $d$ . A reducing atmosphere of gas may be introduced through the tube  $h$ . The whole is enclosed in a Fletcher gas furnace  $F$ . Gas enters through  $A$ , and the products of combustion escape at  $D$ .

The question naturally arises—How far may the indications



afforded by the air thermometer be trusted? Are the degrees indicated by it at a white-heat comparable with the degrees of the ordinary thermometer?

The author believes that the laws of Boyle and of Charles will probably hold good at the high temperatures of ordinary furnaces; and, further, the evidence as to temperature indicated by the air thermometer does not rest upon the expansion of a single gas, as the porcelain bulb may be filled with nitrogen, oxygen, or carbonic anhydride. The question as to the degree of confidence which may be reposed in the numerical values of high temperatures is, however, so important that the author would refer to the following experiment of Carl Barus, who has devoted years of patient work to pyrometric investigations.

Fig. 75 shows the arrangement adopted by him for comparing directly the air thermometer with the thermo-junction.<sup>1</sup> The latter is inserted in a tubulure extending to the centre of the bulb *e*, and the disposition of the various parts of the apparatus

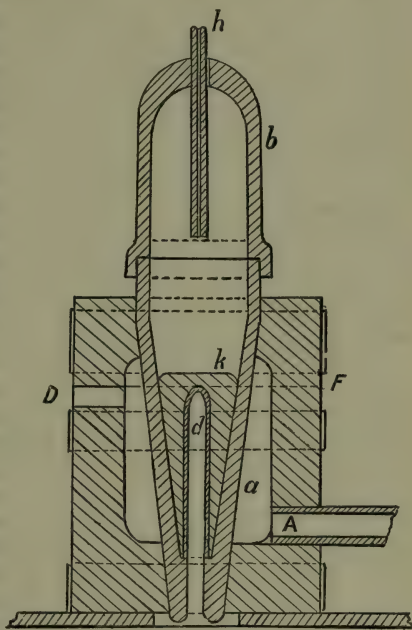


FIG. 74.

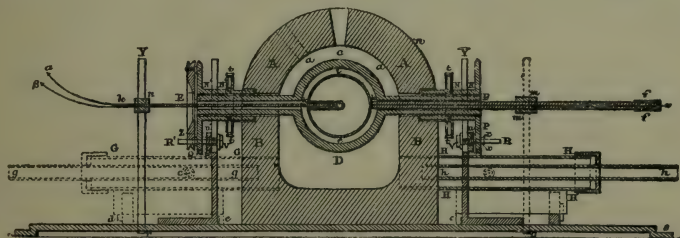


FIG. 75.

is as follows. The walls of a cylindrical furnace *B B* are covered with a hemispherical dome *A A*. The furnace is heated by gas, introduced through the burners *G G*, *H H*; compressed air enter-

<sup>1</sup> *Bulletin United States Geological Survey*, No. 54, Washington, 1889.

ing by the inner tubes *gg* and *hh*. The inlets for the gas are *c c'*. The furnace can be heated to a high temperature with ease; but in order to equalise the heat, Barus employs an internal globular "muffle," *ECDF*. It consists of two hemispheres of fire-clay, provided with lateral tubes, which pass through the walls of the furnace. The two hemispheres are held together by the iron collars *NN*, *NN'*. The outer edges of these collars *P P'* are flanged, and fit into the grooves of two friction rollers *QQ'*, of which *RR'* are the respective axes. There are adjusting screws at *V V'*, *uu'*, *tt'*. The muffle is rotated by a belt pulley screwed on to the flange *P'*. The air thermometer is shown in position, *ffk i e*, supported by the clamp *mm*. A similar clamp *nn*, on the opposite side of the furnace, supports the thermo-junction *kk*, the wires of which are shown at *a β*. It will be observed that the thermo-junction passes directly into the re-entering tubulure of the porcelain bulb; but the wires must not touch the walls of the tubulure. The capacity of the bulb *e* is about 300 c.c. The muffle is turned at the rate of about fifty revolutions per minute; and this speed, which is probably needlessly high, ensures uniformity in the temperature of the furnace.

It will be evident that the arrangements briefly described above enable the indications of the air thermometer and the thermo-junction to be compared, and full details of the experiments will be found in the monograph by Barus. The results of recent work in this direction have been published by the author<sup>1</sup> and also by Stansfield.<sup>2</sup> It will be found<sup>3</sup> that if the results of the experiments be plotted with the electro-motive force of the thermo-junction (in micro-volts) as abscissæ, and the temperatures, indicated by the air thermometer, as ordinates, the several observations coincide very nearly with a straight line; and singularly valuable information is thus afforded as to the trustworthy character of the respective methods. The general conclusion would appear to be—that the thermo-junction, the use of which is very simple, may replace the air thermometer, which, as arranged for accurate work, involves the employment of cumbersome apparatus and much tedious calculation, and is, in fact, about the last piece of apparatus that should be offered to engineers with a view to the measurement of temperatures in the ordinary course of work.

An air thermometer in a form adapted for industrial use has, however, been devised by Prof. Wiborgh of Stockholm,<sup>4</sup> who measures the pressure exerted by the expansion of a known volume of air when forced into a porcelain bulb raised to the temperature which it is required to determine. Another form

<sup>1</sup> Alloys Research, 4th Reports, *Inst. Mech. Eng.*

<sup>2</sup> *Philosophical Magazine*, July 1898.

<sup>3</sup> *Bulletin U.S. Geological Survey*, No. 54, Washington, 1889.

<sup>4</sup> *Journal of the Iron and Steel Institute*, 1888, vol. ii. p. 110.

has recently been patented by Prof. H. L. Callendar,<sup>1</sup> who has so modified the differential air thermometer as to enable the degrees of temperature to be read directly on a graduated tube.

The Uehling Pneumatic Pyrometer<sup>2</sup> is much used in large iron and steel works in America, and has been adopted in this country to a considerable extent for taking the temperature of the blast. This pyrometer is based on the laws governing the flow of air through small apertures, and the principle may be illustrated by fig. 76.

The chamber C has an inlet aperture A and an outlet aperture B, and a uniform suction is created in the chamber C' by the steam aspirator D. Air will be drawn into chamber C' creating

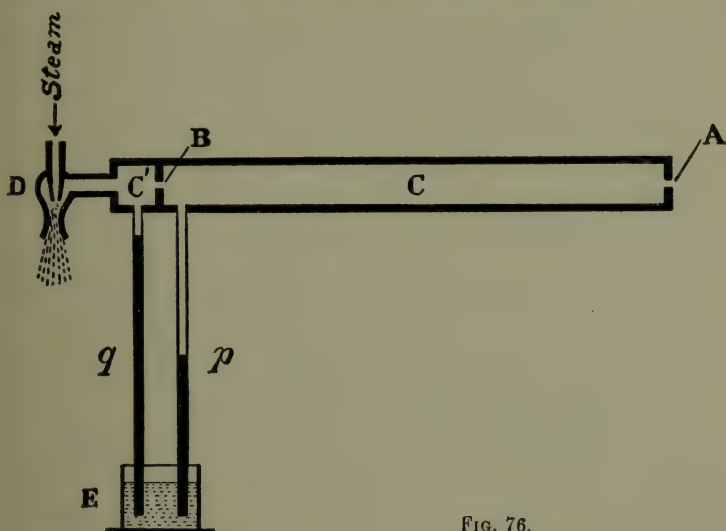


FIG. 76.

a suction in C, which in turn causes air to enter through A. The velocity at which the air flows through A depends upon the suction in C, and the velocity at which it flows through B depends upon the excess of suction in C' over that in C, that is, the effective suction in C'.

As the suction in C increases, the effective suction in C' must decrease, and hence the velocity at which air flows in through A increases and the velocity at which air flows out through B decreases, until the velocity of flow through both apertures becomes equal. When this occurs no further change of suction in C will take place. Air is expanded by heat, and the higher the

<sup>1</sup> *Proceedings of the Royal Society*, 1892, vol. 1. p. 247.

<sup>2</sup> This account is taken from the excellent description by Mr Harrison in *Journ. Iron and Steel Inst.*, 1904, i. p. 124.



temperature the greater will be its volume and the smaller will be the quantity drawn through a given aperture by the same suction after it has been reduced again to normal temperature. If, therefore, the atmospheric air before entering A is heated and again cooled to some lower temperature, say  $100^{\circ}\text{C}$ ., before passing through B, less air will enter through A than is drawn out through B, hence the suction in C must increase and the effective suction in C' decrease, therefore the velocity of air through A will increase and that through B will decrease, until again the same quantity of air flows through each aperture.

Thus, every change in temperature of the air entering through A will cause a corresponding change in suction in C, and these changes in suction will truly represent the changes in temperature of the air entering A. Two manometer tubes  $p$  and  $q$  communicate respectively with C and C', the lower ends being immersed in water. The column in  $p$  will indicate the suction in C', and the column in  $q$  will indicate the suction in C.

In order to make use of the above principle in the construction of an instrument for measuring high temperatures, the following conditions must be fulfilled:—

1. The air must be drawn through the apertures with a perfectly uniform suction.
2. The aperture A must be placed in such a position that the air entering it will have acquired the same temperature as that to be measured.
3. The parts exposed to the heat must be made of a material which will resist the highest temperature to be determined, and at the same time will not scale.
4. The aperture B must be placed in a medium of perfectly constant and fixed temperature.
5. All apertures must remain perfectly clean and free from scale.
6. The chamber C must be absolutely air-tight, so that no air can enter except through A.

The complete pyrometer is shown diagrammatically in fig. 77.

Fig. 78 is taken from a photograph, and shows a portable fire tube and a Steinbart recording gauge. In fig. 77, H is the suction regulator which provides uniform suction, and works on the principle of sucking air through a constant column of water, and by keeping the water-levels in H and N at constant heights a perfectly uniform suction is obtained. The interior of the fire tube and pipe is shown in  $e, f, g, h, i$ ; (figs. 77A and 77) the aperture A is made at the end of a small closed platinum tube  $e$ , enclosed in an outer tube of the same material  $d$ , so that the aperture is within a very small distance of the tube  $d$  which protects it. These platinum tubes are brazed into drawn copper tubes  $c$  and  $f$ , which are cooled by the water jacket F. Atmospheric air enters by connection  $b$ , which opens into the space



between the inner and outer tubes and finds its way to aperture

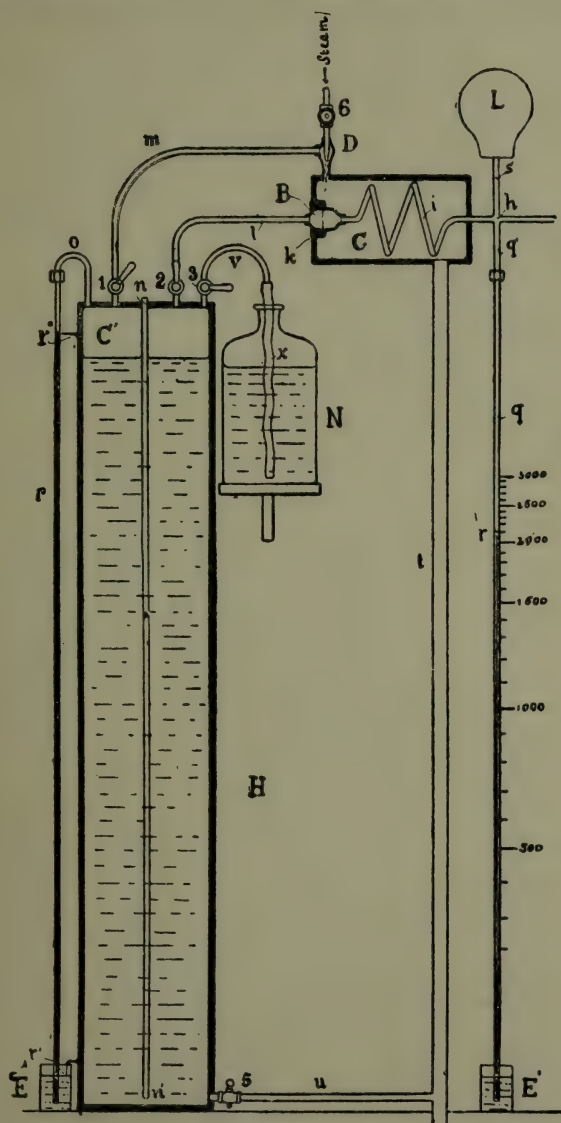


FIG. 77.

A. The fire-tube is held by a sneck in the water-cooled jacket F, which is continuously fed by water which enters at *y* and

escapes at *z*. This water-jacket is screwed into a flange bolted on to the blast or gas main, and protects those parts of the fire-tube which would otherwise be injured by heat. It will thus be seen that by fixing the fire-tube in such a position that the platinum point is in the hot blast or gas, the temperature of which it is desired to measure, the air between the two platinum tubes will acquire that temperature before it enters the aperture A.

The aperture B (fig. 77) is made in a small dished platinum plate, which is held between knife-edge spigot joints in a small brass casting located within a chamber C, and in connection with a copper coiled pipe *i*, which is kept at a temperature of 100° C. by means of the steam from the aspirator D. The air, before entering the fire-tube, is filtered by passing through a 2-inch diameter pipe filled with cotton-wool I (fig. 77A). The steam aspirator D (fig. 77)

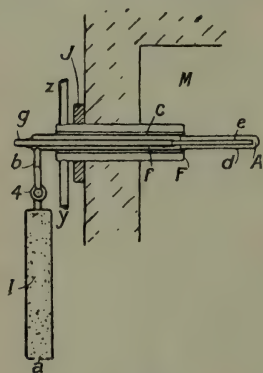


FIG. 77A.

sucks air through the tube *m* out of the chamber C', and produces a suction in C' which is shown by the manometer tube *p*. With a constant suction in C', and cocks 2 and 4 open, air will enter the filter I, where it is purified, and passes through *b* to the fire-tube. It flows in the annular space between the two tubes *c* and *f*, and as it reaches the point of the platinum fire-tube *d*, which protrudes beyond the water-jacket, it acquires the temperature surrounding it which is to be measured, and passes in through the aperture A at that temperature. It then passes through the pipe *e*, *f*, *g*, *h* into the coil *i*, where it assumes the temperature of 100° C., at which it passes through the aperture

B, thence by the pipe *l* into the chamber C', from which it is drawn by the aspirator D through *m*, and discharged with the exhaust steam and water to the atmosphere again. The branch pipes S and *q'* connect respectively to the recording gauge and the manometer tube *q*, which is placed on a graduated temperature scale. This pyrometer is made in either single or double form; in the latter, one temperature and suction regulator and one aspirator serve for two fire-tubes.

A Steinbart Recording Gauge is generally used in connection with this pneumatic pyrometer. This gauge is shown in fig. 79, and consists of a vertical glass cylinder containing mercury, in which floats a glass bell having attached to it a rod with a properly adjusted balance weight.

To this hanging rod is attached a small horseshoe magnet carrying a pen supplied with ink. A small bar of soft iron is

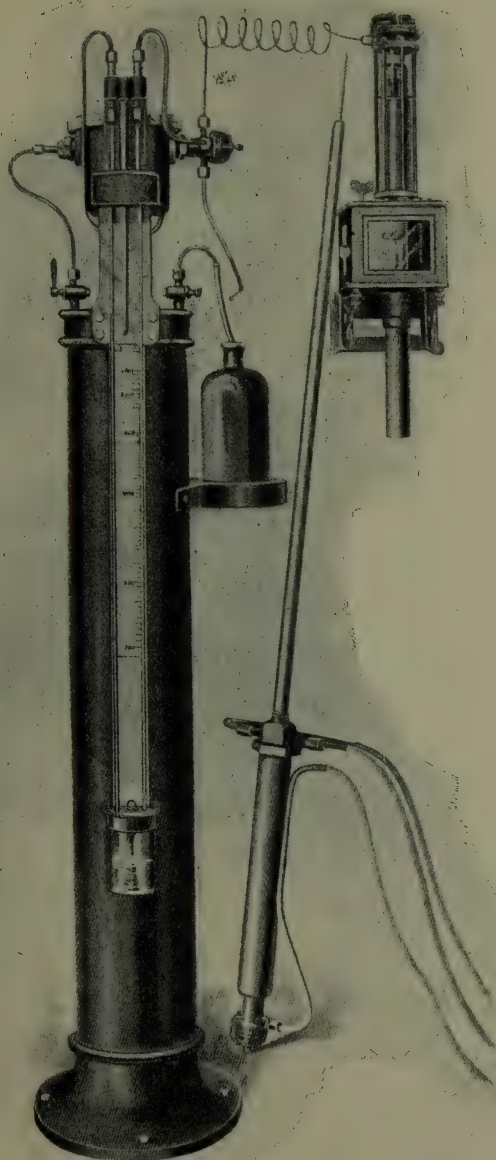


FIG. 78.

placed so as to draw the pen against a continuous strip of paper moved slowly past it by clockwork.

The paper is previously printed with vertical time division lines, and before it reaches the pen it is rolled between two rollers,

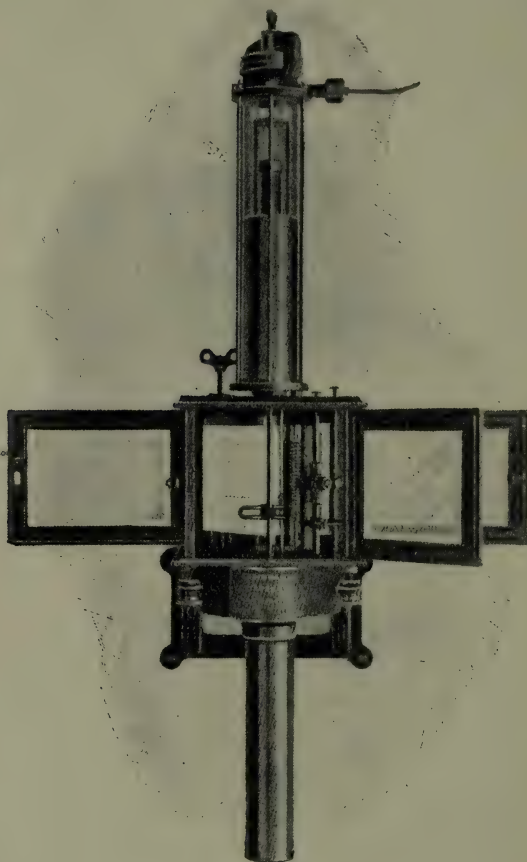


FIG. 79.

one a plain one and the other having on it a series of flanges carefully spaced, which print the horizontal temperature division lines on the paper as it passes, ink being applied by a pad revolving against it. The paper, after passing the pen, winds automatically on to a spring receiving roller, which can be released and the record examined at any time without interfering with the opera-



tion of the gauge. An eight-day clock gives motion to the paper.

Atmospheric pressure is admitted inside the glass float, and the upper part of the inside of the glass cylinder referred to is in connection with the air-pipe from the fire-tube to the regulator, so that the same amount of tension or suction is applied in this glass cylinder as in the air-pipe. This suction lifts the glass float more and more out of the mercury in which it floats as the suction increases, and allows it to fall as it decreases, and the hanging rod, with its attached magnet and pen, rises or falls with it, and thus a line is traced upon the paper, which, being moved by the clockwork, takes various forms as the suction varies, which is a true index of the variations of the temperatures being measured. The pen is set to the temperature line corresponding to the temperature being registered by the regulator, and when once correctly set will continue to rise and fall with variations in temperature. The record paper is usually cut off every twenty-four hours; the last seven hours are always in view. This recorder is very accurate and extremely sensitive, and is very little affected by vibrations. The pneumatic pyrometer is reliable up to  $2500^{\circ}$  F. ( $1425^{\circ}$  C.), and temperatures up to  $3000^{\circ}$  F. ( $1650^{\circ}$  C.) can be measured by it. By its intelligent use the attendant is able to keep the temperature within a few degrees of the heat ordered by the manager, and the latter can always know whether his instructions have been carried out or not.

#### OPTICAL PYROMETRY.

In conducting researches, the thermo-junction possesses, in the author's opinion, many advantages; but, unfortunately, its use involves appliances which are not sufficiently simple to be entrusted to ordinary workmen; and, as Prof. Le Chatelier has pointed out, the use of the thermo-electric pyrometer is only possible in works where the manager or some other responsible person has a taste for scientific investigation, and devotes himself personally to it. In this country such cases are now numerous, and the author would cite as an instance the Clarence Works, where Sir Lowthian Bell established a system of electrical pyrometry in connection with the hot-blast mains, each of which may, in turn, be placed in pyrometric communication with a central office.

A less complicated but still trustworthy instrument of moderate accuracy was much needed, and Le Chatelier supplied it. The eye of the workman again becomes the pyrometer, but it is supplemented by an instrument which enables him to record the intensity of the radiations emitted by a glowing body; so that the old method of judging temperature by the appearance of the mass is rendered comparatively accurate, and the familiar indications of "redness," "bright redness," and "whiteness" are subjected to

direct measurement. Optical pyrometry is not new, but its history, which would include references to the honoured names of Pouillet, Ed. Becquerel, Crova, and Violle, is far too complex to be dealt with in this work.

Mr Crova<sup>1</sup> actually employed his spectro-pyrometer for industrial work, and measured the temperature of certain furnaces at the Creusot Works.

Le Chatelier's<sup>2</sup> photometric instrument is shown in figs. 80 and 81, and in its construction he has utilised the photometer of M. Cornu. The author was indebted either to Le Chatelier's published papers, or to descriptions which he furnished, for the

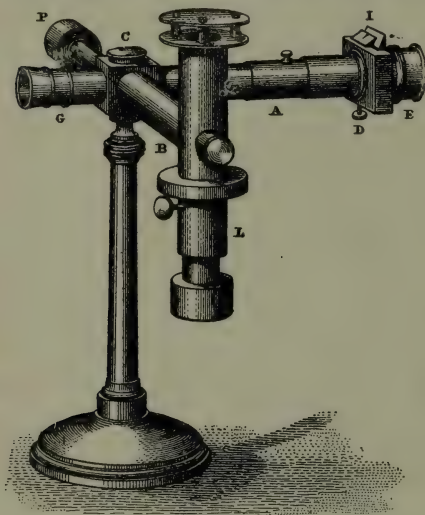


FIG. 80.

details respecting the instrument which will now be given. The light from a standard flame, or lamp L, burning amylac acetate, is reflected to the eye of the observer by the mirror M, while the light from the incandescent body also passes to his eye through a red glass in the eyepiece G; this renders the radiations nearly monochromatic. There is an adjustable orifice at O by which the amount of light admitted from the luminous body can be regulated. In order that intensities, which

may often vary from 1 to 1,000,000, may be compared, absorbent glasses are employed; and these glasses are superposed at O' and E, in greater or less number, as may be necessary. P is a counterpoise, to equalise the weight of the other parts of the appliance. The luminous object, the temperature of which has to be determined, may be focussed by sliding the tube A'; and in order to measure the intensity of its radiations with this instrument, the procedure is as follows:—The position of the mirror M, fig. 81, must be regulated by three screws at C, fig. 80, so that the luminous image of the lamp and that of the object

<sup>1</sup> *Comptes Rendus*, vol. lxxxvii., 1878, pp. 322 and 979; *ibid.*, vol. xc., 1880, p. 252; *ibid.*, vol. xcii., 1881, pp. 36 and 707; *ibid.*, vol. cxiv., 1892, p. 941.

<sup>2</sup> *Comptes Rendus*, vol. cxiv., 1892, p. 214; *l'Industrie Électrique*, No. 7, 1892, p. 147, where the formulæ given in this paper will be found.

to be measured are brought into juxtaposition, being divided by the edge of the mirror.

The photometer depends upon the adjustment to the same brightness of two images, one being that of the flame of a standard lamp, and the other that of the object whose temperature is to be determined. The adjustment is made by means of a diaphragm formed of two plates, each with V-shaped notches opposite to one another. The two plates can be moved past one another by turning a milled head D, fig. 80, and in this way a square aperture of variable size is formed, which, being placed in front of the object-glass O of the telescope, controls the amount of light admitted from the luminous object.

A divided scale I is attached to one half of the diaphragm and a pointer to the other, and this gives directly a linear measurement  $n$  of the aperture.

Let  $n'$  be a measurement when the image of an object of unit brightness (a candle flame, for instance) is matched to that of the standard lamp, and  $n$  the measurement when another object is matched in place of the candle. Since the eyepiece has a red glass within it, only red rays pass to the eye for measurement, and the intensity,  $I$ , of these red rays emitted by the second object, as compared with those from the candle, will be given by the equation

$$I = \left( \frac{n'}{n} \right)^2.$$

But if the two objects are not at equal distances from the instrument, the intensity will be apparently less for the more distant one, in the ratio  $\left( \frac{f}{f'} \right)^2$ , where  $f$  and  $f'$  are the focal lengths (given on the tube A) of the two objects; hence—

$$I = \left( \frac{n'}{n} \right) \times \left( \frac{f}{f'} \right)^2.$$

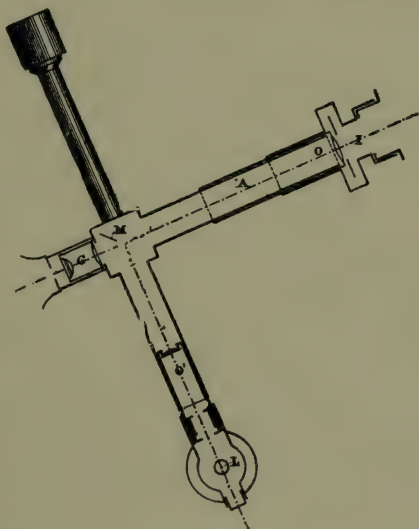


FIG. 81.

As has been already stated, the great differences of intensity which have to be measured occasionally render it necessary to absorb some of the rays from the object or from the standard lamp, as the case may be. This is done by inserting neutral-tinted glasses in suitable holders, either at E or F. Let  $N'$  be the linear measurement of the aperture when the luminous object, shaded by a neutral-tinted glass, is matched with the standard lamp, and let  $N$  be a similar measurement when the same object is unshaded.

Then the coefficient of absorption of the glass  $K$  will be given by the equation

$$K = \left( \frac{N'}{N} \right)^2;$$

and when  $p$  thicknesses of the neutral glass are before the object, whilst the standard glass is left unshaded,

$$I = \left( \frac{n'}{n} \right)^2 \left( \frac{f}{f'} \right)^2 \left( \frac{1}{K} \right)^p.$$

On the other hand, for measuring very low temperatures, when the standard lamp is shaded by  $p$  thicknesses of glass, and there are no glasses before the diaphragm, the formula becomes

$$I = \left( \frac{n'}{n} \right)^2 \left( \frac{f}{f'} \right)^2 K^p,$$

the index  $p$  being required because each glass cuts off a fraction of the light received by it.

Experiments indicate that the change in intensity of the red rays from a body of temperature  $T$  is approximately given by the equation

$$I = 10^{6.7T - \frac{3210}{T}},$$

where  $T$  is reckoned from absolute zero, so that  $T = (t^\circ \text{C} + 273)$ ,  $t$  being the actual reading of the thermometer. This formula has been used to calculate the numbers given in the following table—

Temperature. Centigrade.	Intensity of Red Rays.
600° . .	0.00008
800 . .	0.0046
1000 . .	0.078
1200 . .	0.64
1400 . .	3.35
1600 . .	12.9
1800 . .	39.0
2000 . .	93.0

—the unit intensity being that of the axial zone of the flame of a standard candle.



In one instrument, where  $n'$  (the reading obtained with a candle flame as a luminous object) was 5·2, and  $\frac{1}{K}$  had the value  $\frac{1}{25}$ , the following figures were obtained by Prof. Le Chatelier :—

Temperature.	One Glass before Stan- dard Lamp.	No Neutral Glasses.	One Glass before Diaphragm.	Two Glasses before Diaphragm.
Centigrade.				
700°	39·5			
800	15·2			
900	7·4			
1000	3·8	19·2		
1100	...	10·8		
1200	...	6·7		
1300	...	4·2	21·2	
1400	...	2·7	13·8	
1500	...	...	10·1	
1600	...	...	7·4	
1700	...	...	5·6	
1800	...	...	4·3	21·5
1900	...	...	...	17·0
2000	...	...	...	13·8

But, inasmuch as the emissive power of different bodies for red rays is not the same under like conditions as to temperature, it will be doubtless preferable to calibrate the instrument directly by comparing it with a little mass of platinum, or of iron, which can be maintained at known temperatures as measured by a thermo-couple.

The Féry *absorption* pyrometer, which is an improved form of the optical pyrometer of Le Chatelier, has been found extremely useful for measuring the temperature of very hot but small bodies. It consists essentially of a telescope DB, fig. 82, which carries a small comparison-lamp E, attached laterally. The image of the flame of this lamp is projected on a mirror F at 45°, placed at the principal focus of the telescope; the mirror is only silvered over a narrow vertical strip *ab*, fig. 82A. The telescope is focussed on the object the temperature of which it is desired to measure, this object being viewed on either side of the silvered strip. A pair of absorbing-glass wedges C and C<sub>1</sub> are placed in front of the objective of the telescope, and these wedges are moved laterally by means of a micrometer screw until the light from the object under observation is made photometrically equal to that emitted by the standard lamp E. An auxiliary dark glass D is also fitted, to enable the instrument to work over a higher range of temperature. A table is necessary in order to convert the readings obtained by the scale into

degrees Centigrade or Fahrenheit. Fig. 82A shows the telescope focussed on a small crucible, the narrow vertical silvered strip *ab* being clearly shown.

The Wanner Optical Pyrometer<sup>1</sup> depends for its success on the law determining the relationship of the rays of light to the heat emitted by an incandescent body, as enunciated by Wien and Planck. Thus, for the quantity of light radiated from a hot body, it is possible to gauge the temperature. The light under observation enters through a slit and, after traversing lenses and a prism, forms a spectrum from which, by means of a diaphragm, a small region in the red is cut off for use. The intensity is measured by polarisation. A small electric, incandescent, 6-volt

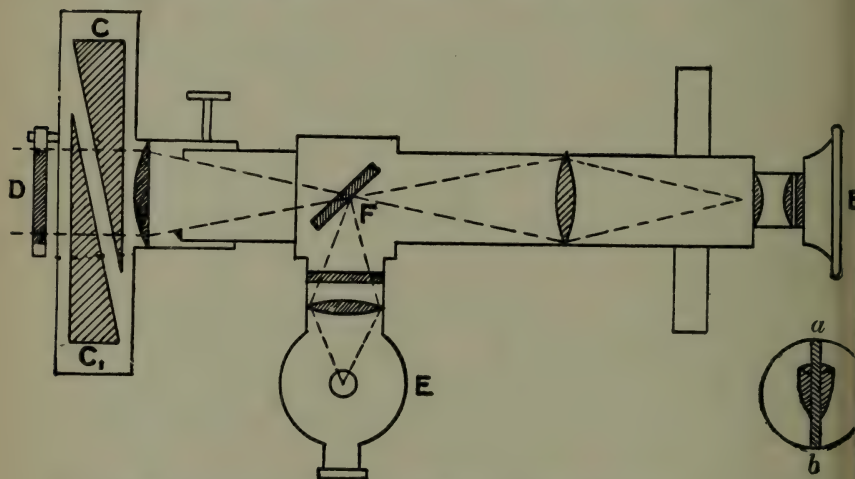


FIG. 82.—Diagrammatic Arrangement of Fery Absorption Pyrometer.

FIG. 82A.

lamp is attached to that end of the apparatus which is directed towards the light under observation, and the light from this is also admitted to the apparatus, and utilised for the purpose of comparison with the intensity to be measured. On looking through the apparatus, the circular field of vision is seen to be divided into two halves, one of which is illuminated by the little electric light, and the other half by the light of the body under observation, the coloration being red. By inserting a rotating eyepiece containing a Nicol prism, the intensity of the two halves of the field of vision is easily equalised. The angle of rotation is measured on a circular scale, and by reading the angle, the temperature corresponding to it is found in the table which

<sup>1</sup> This account is taken from the description prepared by Dr A. Weiskopf (Hanover), *Journ. Iron and Steel Inst.*, 1904, i. p. 140.

accompanies every instrument. The method merely consists in comparing the rays of a known temperature emitted by the electric lamp with the rays of an unknown temperature, and the operation is extremely simple. The apparatus is made in the form of a telescope, and the distance from the object, the temperature of which is to be measured, is of little importance, provided the field of vision is fairly filled by the light. It is essential that the standard electric light should always have the same temperature, and to avoid discrepancies it is occasionally standardised against an amyl-acetate flame.

On comparing the intensity of a certain colour apart from considering the changes of colour of a glowing body at rising temperatures, that is to say, a small section of the spectrum, it is found that with increasing temperature the strength of the rays increases very considerably. For example, if one shuts out of the spectrum all the light from a glowing body, with the exception of the narrow portion corresponding to the Fraunhofer line C, and if one assumes the intensity of this red light when at the temperature of  $1000^{\circ}$  C. to be equal to 1, by the time the temperature reaches  $1200^{\circ}$  C. the intensity is 10 times greater; at  $1800^{\circ}$  C. 804 times greater, and at  $2000^{\circ}$  C. 2134 times greater. If  $I$  represents the intensity of the rays observed,  $T$  the absolute temperature,  $\lambda$  the wave-length of the portion of the spectrum used,  $c_1$  and  $c_2$  two constants, and  $e$  the base of the natural logarithm, the following is the equation which connects the values—

$$I = \frac{c_1}{\lambda^5} \cdot e^{-\frac{c_2}{\lambda T}}.$$

This is Wien's formula, but it is subject to a certain limitation, inasmuch as it only applies to so-called absolutely dark bodies. An absolutely dark body absorbs all light which falls on it, and the nearest approximation to a theoretically dark body is soot. Bright platinum reflects much light and absorbs little, and is therefore the antithesis of the dark body. Iron in the incandescent state scarcely reflects at all, consequently it closely approximates to the properties of the dark bodies. According to Kirchhoff, a theoretically dark body is a hollow space entirely surrounded by walls which are impervious to heat and perfect reflectors. The same effect would be obtained if, instead of the walls being reflecting, they were of the same constant temperature as the hollow space. By making a small aperture in the wall, the radiation is not altered in a measureable degree; it remains, in fact, absolutely dark. It will be readily seen from this that in all closed furnaces the necessary conditions are fulfilled, and in almost every case of a glowing solid or liquid body the law may be taken as correct, since, even when the body is at first not theoretically dark, it approximates more and more to the dark

state as it grows hotter, so that the difference is practically negligible. The determination of the temperature of colourless flames cannot be effected by the optical pyrometer, for the reason that the radiation of the flame differs so greatly from the radiation of a dark body that the law of Wien is no longer applicable. Nevertheless it is possible to ascertain the temperature of the Bessemer converter from the light radiated by the escaping gases.

It is, of course, impossible to express the intensity of light scientifically in any given measure, for the reason that no such measure exists. Consequently it is only possible to compare two intensities with one another. If the standard of comparison be  $I_0$  and the corresponding absolute temperature  $T_0$ , then, from equation given above,

$$I_0 = \frac{c_1}{\lambda^5} \cdot e^{-\frac{c_2}{\lambda T_0}}$$

and

$$\frac{I}{I_0} = e^{-\frac{c_2}{\lambda} \left( \frac{1}{T} - \frac{1}{T_0} \right)}$$

If  $I_0$  and  $T_0$  are known in this equation, that is, the standards for measurement, and also  $I$  and  $c_2$ , then  $T$  alone remains unknown and can be calculated.

The construction of the optical portion of the pyrometer is illustrated in fig. 83.

At  $S_1$  are two slits  $a$  and  $b$  placed vertically one above the other;  $O_1$  is a lens fixed at a point equal to its focal distance from  $S_1$  which makes the rays parallel.  $K$  is a direct vision prism. Every beam passing through  $a$  and  $b$  is dispersed by the spar polariser  $W$  into two polarised parts perpendicular to one another.  $Z$  is a double prism by which the rays on either side are deviated towards the axis.

The rays are collected by the lens  $O_2$  which forms images of  $a$  and  $b$  directly in front of the slit  $S_2$  (the ocular slit), two images of each appearing, owing to the ordinary and extraordinary rays. The dimensions of the prism  $Z$  are so contrived that an image of  $a$  (the ordinary rays) and one of  $b$  (the extraordinary rays) coincide exactly before the slit. It is evident that to form the image of  $a$  in front of the slit  $S_2$  only the upper half of the prism  $Z$  can come into play, while the image of  $b$  can in like manner only be produced by the lower half. Both images are, however, polarised vertically to each other, and the eye behind  $S_2$  therefore views the upper half of  $Z$  illuminated by  $a$  and the lower half illuminated by  $b$ . By means of the revolving Nicol prism  $N$ , either one or other of the images can be intensified or weakened.

The spectroscope is thus composed of the parts  $S_1$ ,  $O_1$ ,  $O_2$ , and  $K$ , while the photometer consists of the parts  $W$ ,  $Z$ , and  $N$ .



The method of reducing the two fields of light from the hot body to be measured and the standard electric light respectively is first to polarise them in planes at right angles to each other, and then the intensity of each can be varied by viewing through a Nicol's prism which can be rotated. This angular rotation of the "Nicol" is then a measure of the intensity of the light, and therefore of the temperature.

There is another optical instrument, the pyrometer devised by Messrs Nouel and Mesuré, and used by the author for some years in the laboratory of the Royal School of Mines. It consists of a quartz plate A (fig. 84) placed between two Nicol prisms, an arrangement that renders it possible to suppress at will the radiations of any particular part of the spectrum by simply rotating one of the Nicol prisms. If a hot body be observed through the instrument, and the prism be rotated by means of the divided head B, the red colour of the body will be seen to change to yellow, then to green, and finally to blue. The angle of rotation necessary to extinguish the red colour varies with the temperature, and serves as a measure of it; but the difficulty of remembering the precise tint by which the instrument was calibrated prevents a high degree of accuracy from being attained in its use.

The Féry *radiation* pyrometer has been found very useful for measuring very high temperatures, as the whole of the instrument is placed outside the high temperature, and it is well known how difficult it is to find a material with which to construct a pyrometer to be maintained for pro-

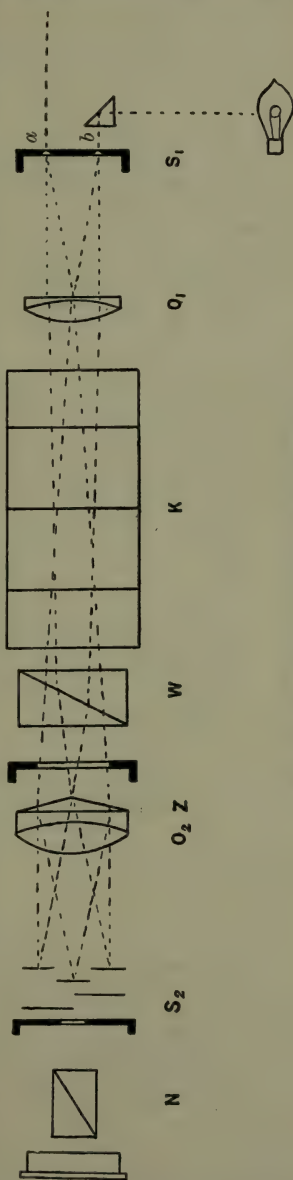


Fig. 83.—Diagram of Wanner Pyrometer.

longed periods at high temperatures without suffering changes in its physical properties.

A further difficulty is introduced by the chemical activities of furnace products and furnace gases, which in many cases render difficult the adequate protection of the resistance wire or thermo-

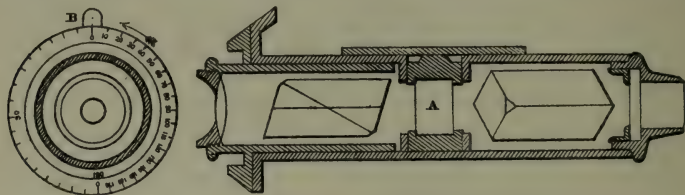


FIG. 84.

couple. In use, the Féry pyrometer is placed at some distance from the furnace, and no part of it is raised above 90–100° C.

In this pyrometer, the radiation which emanates from a hot body, or which passes out through an observation hole in the wall of a furnace, falls upon a concave mirror, and is thus brought to a focus. In this focus is placed a thermo-couple whose temperature is raised by the radiation falling upon it; the hotter

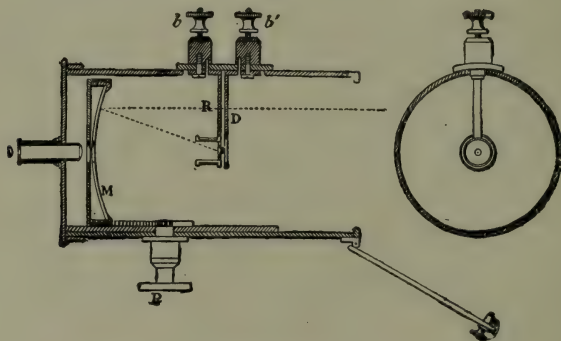


FIG. 85.—Féry Radiation Pyrometer Telescope.

the furnace, the greater being the rise of temperature of the couple.

The complete instrument consists of a telescope and a galvanometer, arranged for direct reading or for photographic or autographic recording. The telescope (fig. 85) has fixed within it, at a point upon its optic axis, a copper-constantan thermo-couple, arranged in the form of a cross. The two wires are attached to two brass strips D and R, which are attached to the terminals *b b'*.

These terminals are connected by leads to the galvanometer.

When used for measuring the temperature of a furnace, an observation hole in the wall of the furnace is sighted through the eyepiece O, the image of this hole being brought into coincidence with the thermo-junction.

It is necessary that the image of the observation hole should slightly overlap the junction which appears to the eye as a black disc in the centre of the field of view. The readings of the instrument are then independent of the size of the observation hole. The image of the hole is reflected to the eyepiece O by two mirrors placed close to the couple. These mirrors serve for the adjustment of focus; they are so arranged that the image of the hole appears to be split into two parts, which only coincide when the focussing is correct. The image thus formed upon the junction produces a rise of temperature which has been shown experimentally to be proportional to the amount of radiant energy which enters the telescope. The junction acquires exactly and with great rapidity the temperature of the image. The electromotive force which is thus generated is measured by the ordinary methods, and the Thread Recorder (p. 178) is very largely used in connection with this pyrometer for recording the temperature of furnaces, etc. Temperatures as low as  $600^{\circ}$  can be read, but the instrument is most useful for high temperature work.

The graduation of the galvanometer scales, either direct-reading or recording, is based upon the *Stefan-Boltzmann radiation law* which expresses the relation between the temperature of a body and the amount of radiant energy which it emits. The law is as follows: "The radiant energy emitted by a black body is proportional to the fourth power of the absolute temperature of the body," or

$$E = K(T^4 - T_0^4),$$

where  $E$  is the total energy radiated by the body at absolute temperature  $T$  to surroundings at absolute temperature  $T_0$ , and  $K$  is a constant depending on the units used.

This law has received abundant experimental support throughout the widest range within which temperature measurements can be made.

As indicating the precision to be attained with the Féry Pyrometer over the range of temperatures independently controllable with a thermo-couple pyrometer, some data obtained by M. Féry, and reproduced by Messrs Waidner and Burgess in Bulletin No. 2 of the Bureau of Standards, Washington, U.S.A., may be given. In the investigation referred to, the Stefan-Boltzmann Law was assumed to hold in the form

$$CE = d = 7.66T^4 \times 10^{-12},$$

where  $E$  is the total energy of radiation,  $d$  the galvanometer deflection,  $T$  the absolute temperature, and  $C$  a constant.

<i>d.</i>	Temperature from Thermo-couple.	Temperature from Stefan's Law.	$\Delta$ in Degrees.	Error in Percentage.
11.0	844°	860°	+ 16°	1.85
14.0	914	925	+ 11	.84
17.7	990	990	0	.0
21.5	1054	1060	+ 6	.60
26.0	1120	1120	0	.0
32.2	1192	1190	- 2	.17
38.7	1260	1250	- 10	.80
45.7	1328	1320	- 8	.60
52.5	1385	1380	- 5	.36
62.2	1458	1450	- 8	.50

If the galvanometer used with the pyrometer has a uniformly graduated scale and the temperature  $T_1$ , corresponding to any one scale reading  $R_1$ , is known, that for any other reading  $R_2$  may be found from the relation

$$T_2 = T_1 \sqrt[4]{\frac{R_2}{R_1}}.$$

It is here assumed that  $T_0^4$  is negligible in comparison with  $T_1^4$  or  $T_2^4$ ,  $T_0$  being here the absolute temperature of the thermo-junction at the focus of the telescope.

For very high temperatures a diaphragm is placed in front of the receiving mirror (see fig. 86) to reduce the radiation falling upon it. The radiation in the two cases is proportional to the areas of the respective apertures.

By altering the aperture of the diaphragm and converting the galvanometer readings by means of the formula given above, temperatures far beyond the scale on the galvanometer can be deduced.

The Stefan-Boltzmann Law is strictly true only of "perfectly black" bodies; bodies, that is, which absorb all the radiation falling upon them, and are destitute of reflecting power. Some bodies conform so nearly to this definition that no appreciable error is introduced by treating them as perfectly black, and by taking their true temperatures to be given by the readings of a Féry pyrometer, sighted and focussed upon them. Such substances are coal, carbon, and those metals which, on being heated, become coated with a black oxide; for example, iron and copper.

But a far larger class of *effectively black* bodies is furnished by enclosed furnaces, muffles, combustion chambers, and the like. When the interior of such a furnace or chamber is at nearly the same temperature throughout, and when the observation hole is



only of moderate dimensions compared with the distance behind it of the nearest furnace wall or solid body, the radiation issuing through the hole is independent of the quality of the radiating surfaces, and is the same as if those surfaces were perfectly black.

Flames interposed between the observation hole and the solids behind, provided they are at the same temperature as the furnace, will not alter the case in the least. But even when their temperature differs from that of the furnace, such flames are too transparent to absorb or emit any perceptible radiation, so that in practice no error arises from this cause. When the pyrometer is sighted upon a body which is neither black nor the effectively black interior of a furnace, the temperature directly read off

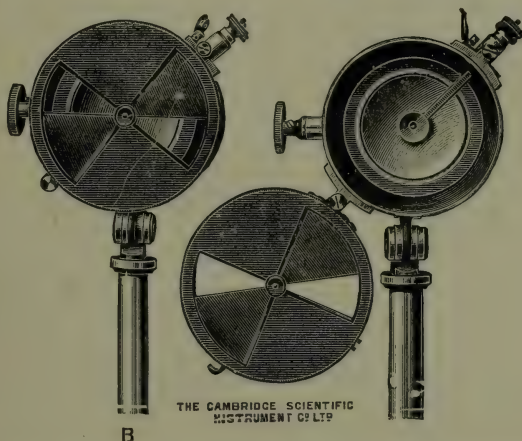


FIG. 86.—Féry Radiation Pyrometer, showing Diaphragm for reducing Aperture of Telescope.

from the scale of the galvanometer will be *lower* than the true temperature of the body. This uncorrected reading is called the *black-body temperature* of the body observed, and the greater the reflecting power of the body, the more widely does the black-body temperature differ from the true temperature. As an example it may be mentioned that if the “black-body temperatures” of carbon and platinum are equal, their actual temperatures may differ considerably ( $180^{\circ}$  C. or so, at  $1500^{\circ}$  C.).

Transparency of the observed body would further tend to increase the discrepancy, but in any practical case the thickness of the body in the line of sight would be sufficient to ensure opacity, so that the error thus arising would not be perceptible.

In practice, if the true temperature be required instead of the black-body temperature, it will be necessary to apply corrections,

based on independent investigation, the data being in some cases already available. On the other hand, *for any given substance with its surface in a specified condition, the black-body temperature serves just as certainly and definitely as the true temperature to define the thermal state.* It is precisely this certainty and definiteness which is of paramount importance in industrial operations, and in a very large number of cases black-body temperatures will be found the most convenient for specifying the thermal conditions under which a process is to be carried out.

The temperature readings, within limits, are independent of distance, and this is a point which may need further explanation. If it is supposed that the pyrometer is sighted upon a hot body of limited dimensions, the total amount of radiation reaching the aperture of the mirror will vary with the distance from the hot body, and will be inversely proportional to the square of the distance. If, then, the receptive surface of the thermo-junction were sufficiently extended to receive the whole of the radiation which is converged to a focus by the mirror, it might be expected

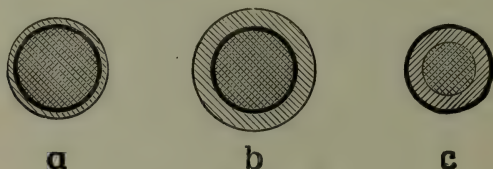


FIG. 87.

that the indications of the galvanometer would fall off as the distance was increased. The thermo-junction, however, is not large enough to receive the whole of the radiation which converges towards it. The real image of the source, formed by the mirror, overlaps the thermo-junction on all sides (fig. 87, a), so that when the source is approached more nearly, thus increasing the size of the image produced, the only effect is to increase the amount of overlapping, while the thermo-junction receives no more radiation than before (fig. 87, b). On the other hand, if the pyrometer is withdrawn to so great a distance that the image formed is too small to cover the thermo-junction completely (fig. 87, c), the readings obtained will be too low, and will become lower and lower as the pyrometer is withdrawn further and further from the source of heat.

From the above it will also be readily understood that when working at any given distance from a hot body, it is necessary for the body in question to be of sufficient size, otherwise the image of the body would be too small to overlap the thermo-junction on all sides. But provided the hot body is large enough to secure the necessary overlapping, no further increase in its dimensions

will add to the amount of radiation actually received by the thermo-junction. The diameter of the hot body (or furnace aperture) should measure as many inches as the distance from hot body to pyrometer measures yards, or, in other words, the aperture should measure in diameter about one-fortieth of the distance the pyrometer is away from the hot body.

#### GENERAL CONSIDERATIONS.

The accurate measurement of high temperatures is increasing in interest, in view of the rapid development of the study of chemical dynamics. It is now recognised that the industrial chemist, as well as the engineer, has to deal with the influence of mass. Many chemical processes are reciprocating, so that the original product may be obtained from the product of the reaction. The result of such opposed processes is a state of chemical equilibrium, in which the original and the newly formed substances are present in definite quantities, and remain the same so long as the conditions, more especially those of temperature and pressure, do not undergo further change. In conducting many operations, temperature and pressure are reciprocal factors; hence the importance of being able to measure with accuracy a bright red heat. Now, as Prof. Le Chatelier has already pointed out, in the production of chlorine by the Deacon process, or in the baking of porcelain, a variation of temperature of only  $20^{\circ}$  may be attended with complete failure of the operation. There is, however, one other case of more direct interest to the engineer in relation to steel. It involves the consideration of the possibility of the occurrence, at high temperatures, of molecular changes in steel, which profoundly modify its mechanical properties, in a way that was indicated on p. 144. It is difficult to describe briefly the nature of this change, but the following statement may be sufficient.

When a mass of steel is cooled from a very bright red heat, say from  $1200^{\circ}$  Centigrade, to the ordinary temperature of the atmosphere, at least three critical points, each attended by an evolution of heat, may be detected by the pyrometric methods already indicated; and their position may be determined very precisely by the aid of the differential method already described and illustrated. The development of the theory of the importance of these critical points is mainly due to Osmond,<sup>1</sup> who has fixed the normal temperatures at which they occur during the slow cooling of a mass of steel in which the notation of Chernoff and of Osmond has been retained.

<sup>1</sup> See Report by the Author to the Alloys Research Committee of the Institution of Mechanical Engineers, *Proceedings*, No. 5, 1891, p. 543, and *Nature*, vol. xli., 1889, pp. 11, 32, where references are given to Osmond's papers.



The author has already stated his belief that these changes are of great importance in modifying the structure, and consequently the mechanical properties, of steel; he shared this opinion with the late Sir W. Anderson, formerly Director-General of Ordnance Factories, who instituted, at Woolwich Arsenal, some interesting experiments bearing on the question. The initial temperature of the mass, and its rate of cooling, are not without influence on the temperatures at which these critical points occur. For instance, in hardening large pieces of steel, such as the "A" tubes of guns, it may happen that, when the mass is plunged into the oil bath, a portion of the metal may be at a temperature below that at which the molecular transformations occur. It is, moreover, only necessary for the temperature of different parts of the mass to vary within a narrow range, in order that the bath may exert different influences on adjacent parts of the steel. This is a matter of great importance; and M. Barba of the Creusot Works began its study in 1880, but abandoned the attempt for want of sufficiently exact and practical methods of measuring high temperatures. The author attacked the problem in 1891, and published the results of the only experiment which had then been made. For the purpose of conducting it, Sir W. Anderson caused an ingot of steel to be prepared, 8 inches high and 4 inches in diameter. It contained carbon 0.799, silicon 0.084, manganese 0.412. A Le Chatelier thermo-junction was placed in a hole drilled to the centre of the mass, and another thermo-junction was fixed in a hole drilled near the surface. The mass was heated to bright redness, the external junction indicating 1100° Centigrade, each thermo-junction being in turn switched into connection with a recording apparatus, and dotted curves representing the cooling of the exterior and at the interior of the mass were thus obtained. The cooling was effected by plunging the mass into water. The effect of rapid cooling on the surface was, of course, to contract it and to compress the mass, the pressure being very marked in the zone of the ingot in which the external thermo-junction was inserted. The result appeared to be a lowering of the critical point (which should have occurred at about 690° Centigrade) to a little over 400° Centigrade.

It would therefore appear that the great problems of chemical equilibrium are applicable to the relations between the constituents of the complex material, steel; and that the pressure exerted on the molecules of a metallic mass must be measured, as well as its temperature, in investigating the molecular grouping of metals, upon which their mechanical properties depend.

It may now be well to indicate very briefly some other directions in which the measurement of high temperatures may be useful. The spent gases from boiler furnaces are often hotter than 400°, and their temperature should, in many cases, be accurately known. In researches on heat engines, complex problems arise



demanding a knowledge of temperatures of about 500°. Foundry practice presents numerous cases, as, for instance, casting guns by the Rodman system; in conducting which it is most important, as Prof. H. M. Howe has pointed out, to be able to measure and control the rate of cooling of the core of the gun, as compared with its outside. By this means it is possible to avoid setting up prejudicial stresses, and to promote the development of useful ones in castings of all kinds. Addy has appealed to the importance of pyrometry in connection with experiments on armour-piercing projectiles; and it will be evident that the use of projectiles and explosives is a branch of engineering fertile in problems, the solution of which must, in a great measure, be based on pyrometry.

The gradual introduction of new alloys is changing the methods of investigation which must precede and govern the use of materials in construction. It may be thought that work of the kind indicated here is not sufficiently practical to deserve the attention of either the metallurgist or the engineer. If fears of this kind should arise, the author would recall the eloquent words addressed by the Director-General of Ordnance Factories to such doubters, who, he says, "can never have been placed in positions of responsibility, where the safety of ships, the lives of their passengers and crews, the efficiency of armaments, and their own financial position were in question; they can never have looked at masses of steel with the view of deciding whether they were fitted for the purpose for which they had been produced; nor can they ever have felt the helplessness, and the want of reasonably secure guidance, which it is still the lot of the responsible judge to experience." The guidance for which Sir W. Anderson appealed can only be afforded by employing to the fullest extent the methods, as well as the results, of physical and metallurgical research.

Since the above was written, the industrial application of pyrometry has extended in almost all branches of our technical industry, and the accurate and systematic determination of temperatures to enable the scientific control of the various operations is in many works a part of the daily routine. In the Royal Gun Factory, Woolwich,<sup>1</sup> a very elaborate pyrometric installation has been fitted, in which the following branches are wired up to, and are under pyrometric control from, the metallurgical laboratory—the heavy forges, including heating and reheating furnaces; the oil-hardening and tempering branches, including various furnaces and baths; the case-hardening shop, the drop forging shop, the lead bath (specimen treatment plant), and the gas muffles throughout the department, used by tool-smiths and other craftsmen. The various sections of the gun department are also in direct telephonic communication with the

<sup>1</sup> Lambert, *Journ. Iron and Steel Inst.*, 1908, No. 1, pp. 109-136.

metallurgical laboratory, and this is found to be a great aid to the use of the pyrometric plant.

In bicycle and motor-car works, where large quantities of special steels are used which require most careful thermal treatment, the value, and even necessity, of pyrometric control is not overlooked, and most of these works are fitted with a more or less efficient plant, wired up to the various departments.

### BIBLIOGRAPHY.

- Sir C. W. Siemens.—*Pyrometers* (Journal of the Iron and Steel Inst., 1871, p. 50).
- T. Carnelley and T. Burton.—*Carnelley and Burton Pyrometer* (Journ. Chem. Soc., 1884, p. 237).
- A. von Bergen.—*Hot Blast Pyrometer* (Journal of the Iron and Steel Inst., 1886, p. 207).
- A. Evrard.—*The Mesuré and Nouel Pyrometer* (Génie Civil, vol. xiii. p. 43).
- C. Barus.—*Historical Account of Pyrometry* (United States Geological Survey Bulletin, No. 54).
- H. M. Howe.—*Methods of Measuring High Temperatures* (Eng. and Min. Journ., vol. xlix. p. 637).
- H. M. Howe.—*The Le Chatelier Pyrometer* (Eng. and Min. Journ., vol. l. p. 427).
- Sir W. C. Roberts-Austen.—*Automatic Methods of Recording* (Journal of the Iron and Steel Inst., 1891, No. 1, p. 90; also 1892, No. 2, p. 33).
- H. Le Chatelier.—*Optical Method of Determining High Temperatures* (Comptes Rendus, vol. cxiv. p. 214).
- B. H. Thwaite.—*Fuel and its Efficiency* (Journal of the Iron and Steel Inst., 1892, No. 1, p. 183).
- H. L. Callendar.—*Platinum Pyrometers* (Journal of the Iron and Steel Inst., 1892, i. p. 164).
- Seger.—*Lecture on Pyrometry* (Berg- und Hütten. Zeit., vol. li. p. 90).
- Sir W. C. Roberts-Austen.—*Instruments for Measuring High Temperatures* (Minutes of Proceed. of Inst. Civil Eng., vol. cx. pp. 152-186).
- Sir W. C. Roberts-Austen.—*The Recording Pyrometer* (Journal of the Iron and Steel Inst., 1893, i. p. 112).
- C. Barus.—*Thermo-electric Measurement of High Temperature* (United States Geological Survey Bulletin, No. 103).
- H. Morton.—*The Uehling and Steinbart Pyrometer* (Engineering, vol. lviii. p. 251).
- C. Alder Wright.—*Pyrometry* (Industries and Iron, vol. xvii. pp. 128, 149, 176, 194).
- C. T. Heycock and T. H. Neville.—*Platinum Resistance Pyrometry* (Journ. Chem. Soc., vol. xlvii. p. 160).
- H. Wedding.—*Various Pyrometers* (Stahl und Eisen, vol. xvi. p. 660).
- Sir W. C. Roberts-Austen.—*Fourth Report of the Alloys Research Committee* (Proc. Inst. Mech. Eng., 1897).
- Sir W. C. Roberts-Austen.—*Industrial Use of Recording Pyrometer* (Journ. Soc. Chem. Ind., vol. xvi. p. 5).
- Bichat.—*Principles of Pyrometry* (Revue Industrielle de l'Est, 1897).
- C. Chree.—*Recent Work in Thermometry* (Nature, vol. lviii. p. 304).
- A. Stansfield.—*Thermo-electric Pyrometry* (Phil. Mag., vol. xlvi. pp. 59-81).
- Uehling and Steinbart.—*The Uehling and Steinbart Pyrometer* (Stahl und Eisen, vol. xix. pp. 431-438).

- L. Holborn and A. L. Day.—*The Gas Thermometer* (Amer. Journ. of Science, vol. x. pp. 171–206).
- H. L. Callendar.—*Measurement of Extreme Temperatures* (Proc. Roy. Inst. of Great Britain, vol. xvi. pp. 97–113).
- W. Rosenhain.—*Pyrometry* (Electro-Chemist and Metallurgist, vol. i. pp. 141, 163).
- G. K. Burgess.—*Translation of Le Chatelier and Boudouard's book on the Measurement of High Temperatures*, 1901.
- H. A. Seger.—*Uses of Seger Cones* (Records of the Royal Porcelain Factory, Berlin, 1902).
- R. S. Whipple.—*Temperature Indicator* (Proc. Phys. Soc., vol. xviii. p. 235).  
— *Pyrometers Suitable for Metallurgical Work* (Journal of the Iron and Steel Inst., 1904, No. 1, p. 98).
- J. A. Harker.—*Pyrometry* (Proc. Roy. Soc., vol. lxxiii. pp. 217–219).
- H. L. Callendar.—*Electric Methods of Measuring Temperatures* (Lecture at Royal Institution, March 1904; Engineering, vol. lxxvii. pp. 336–370, 402–4).
- H. Rable.—*Modern Methods of Measuring High Temperatures* (Chemiker Zeitung, vol. xxviii. p. 39).
- C. W. Waidner.—*Modern Methods of Pyrometry* (Proc. Engineers' Soc. of Western Pennsylvania, vol. xx. pp. 313–402).
- E. J. Batz.—*Methods of Temperature Indication* (Journ. Soc. Chem. Ind., 1905, vol. xxiv. p. 307).
- E. F. Røeber, R. Moldenke, and others.—*Discussion on Pyrometers* (Electro-chemical and Metallurgical Industry, vol. iv. pp. 436–441).
- R. S. Whipple.—*Practical Pyrometry* (Engineering Review, vol. xvii. pp. 148–164).
- T. Swinden.—*Classification and Description of Pyrometers* (Foundry Trade Journal, vol. ix. pp. 5–22).
- G. K. Burgess.—*The Estimation of High Temperatures* (Proc. Amer. Electro-Chemical Soc., 1907, p. 247).
- W. Rosenhain.—*Observations on Recalescence Curves* (Proc. Phys. Soc., vol. xxi. p. 180).
- J. W. Lambert.—*Pyrometric Installation in the Gun Factory, Woolwich* (Journal of the Iron and Steel Inst., 1908, No. 1, pp. 109–136).
- A. Portevin.—*Differential Pyrometry* (Revue de Métallurgie, 1908, pp. 295–305).

## CHAPTER VI.

### METALLOGRAPHY.

**Definition.**—In the widest sense, metallography deals with the composition, constitution, structure, and physical properties of metals and alloys, but is sometimes confined merely to the microscopic examination of these materials, and in this case should be termed microscopic metallography.

**History of Microscopic Metallography.**—In metallurgy, the microscope was first applied to the examination of iron, and the first records go back to 1722, when Réaumur described the structure of a chilled casting under the microscope, and traced the changes of softened cast iron as modified by the elimination of impurities. François, again, so early as 1832, took the interesting case of the direct reduction of iron from its ores, and followed the successive changes by the aid of the microscope. The following passage, translated from this quaint and accurate observer, is full of interest, and might almost have been written by a modern metallurgist:—

“If to these analytical data observations under the microscope with a magnification of 300 to 400 diameters be added, it is seen that ordinary iron is merely a metallic network with a close-grained tissue, with submerged scoriaceous opaline, sometimes subcrystalline, portions, and with little globules and metallic grains ranged in every direction. Sometimes nests of translucent prismatic and bacillary crystals, with metallic portions adhering, are noticed hidden in the paste. These are the grains of steel which can be made to disappear by heating.”

It appears that modern microscopic metallography has been developed from the study of meteoric irons, and, as has often happened in the history of science, it appears to have had several independent origins.

The publications of Dr Sorby go back to 1864, and those of Prof. Martens to 1878, but in spite of this difference in date, the labours of the latter present all the characters of complete originality. While Dr Sorby devoted himself to the



development of a complete method of examining sections of opaque bodies under the highest magnifying powers, and the application of this method to different products of the metallurgy of iron, Prof. Martens first studied, though without neglecting the examinations of sections, the general laws of fractures, fissures, blowholes, and crystallisation in metals. After 1878 the study was carried on, on the Continent and in America, by Osmond, Werth, Wedding, Behrens, Howe, Charpy, and Sauveur, but very little attention was paid to it in this country until about 1890, when Prof. Arnold commenced, and was closely followed by Stead, both of whom published papers before the Iron and Steel Institute in 1894. Since this latter date great strides have been made in this subject, and many metallurgists have devoted much time and thought to the practical and theoretical sides of the science.

At the present time it is not uncommon for metallurgical works and laboratories to be equipped with a complete micrographic and pyrometric plant in addition to ordinary chemical and testing laboratories. As has already been shown, metallic alloys occupy an important place in the industrial world; the character of some of their physical properties (hardness, malleability, fusibility, etc.) cause them to be preferred to pure metals for many purposes; yet, in spite of this extended use, very little was known about their constitution until quite recently. Each improvement introduced was the result of numerous experiments, and not of organised scientific research. Now all this is being altered, and in modern metallography we have the results of systematic research work carried out on metals and alloys by the above-mentioned metallurgists and others.

The chief point proved by these researches is that all the properties of alloys, and therefore their industrial value, depend directly upon two factors:—

1. Their chemical constitution, that is to say, the relative proportions of (a) the component metals, (b) the chemical compounds formed by these metals, (c) the isomorphous mixtures, or (d) the various allotropic modifications of the constituents.

2. Their physical constitution or structure, that is, the shape and dimensions of the crystals of the elementary constituents, which, by their juxtaposition, constitute the metallic mass.

The first aim of a systematic study of alloys must be to ascertain their chemical constitution and structure, and its final aim must be the study of the relation existing between these ascertained factors and their useful properties.

No one of the methods of research hitherto devised is sufficient to solve the problem of the constitution of alloys, and it is necessary to use all the methods by which useful information may be obtained.

The most important methods used are the following :—

1. Chemical methods.—General analysis and separation of constituents.
2. Microscopic methods.—Examination of constitutional and crystalline structure.
3. Thermal methods.—Determination of freezing-points and other thermal changes.
4. Mechanical methods.—Determination of elasticity, tenacity, ductility, resistance to crushing, etc.
5. Electrical methods.—Determination of electrical resistance and electro-motive force.
6. Magnetic methods.—Examination of the various magnetic properties.

Of these methods, the first three are used in conjunction with one another for the preparation of equilibrium diagrams, whilst all are used for the investigation of the useful properties of the alloys.

### Microscopic Metallography.

The following are the chief points ascertainable by the use of the microscope in the examination of metals and alloys :—

*a.* The crystalline state of the material, and changes in the general structure due to varying mechanical or thermal treatment. This is well illustrated by figs. 88 to 93, which show the effect of hard drawing and annealing at different temperatures on brass, the composition of which is Cu 70, Zn 30 per cent. Figs. 94 to 97 also illustrate the difference in structure of an alloy Cu 90 Al 10, when cast in sand, cast in chill, forged and annealed.

*b.* The constitution of the material, that is to say, the differentiation of the various constituents of which the alloys are built up ; this is one of the most important points connected with the study of alloys. This is illustrated in fig. 98, which is a photo-micrograph of an alloy containing tin 83, antimony 11, and copper 6 per cent. The cubic crystals seen consist probably of the compound  $\text{SnSb}$ , while the ragged crystals running through these consist of the compound  $\text{SnCu}_3$  ; these two sets of crystals are contained in a groundmass of eutectic. Fig. 99 shows the constitution of cemented steel slowly cooled down ; the white lines consist of cementite, the carbide of iron,  $\text{Fe}_3\text{C}$ , while the darker groundmass consists of pearlite which, under a high magnification, would be seen to consist of alternate curved plates of cementite and ferrite.

*c.* The presence of foreign bodies, such as slag patches, is illustrated by fig. 100, which shows a number of patches of slag in a low carbon steel. Manganese sulphide in steel, oxides in steels and copper, etc., may also be detected by the microscope.

*d.* Mechanical defects, such as flaws, blowholes, and cracks,

MICRO-STRUCTURE OF BRASS.

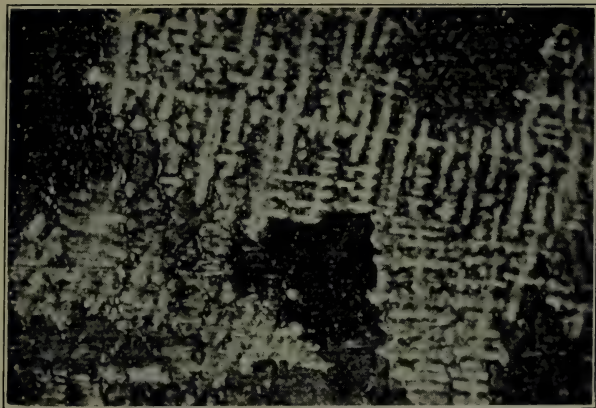


FIG. 88.—As Cast.  $\times 50$  d.

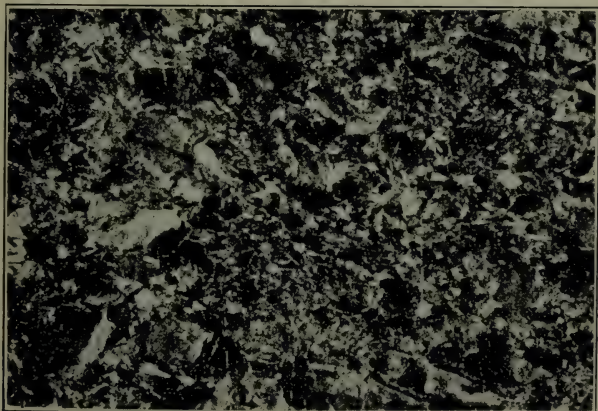
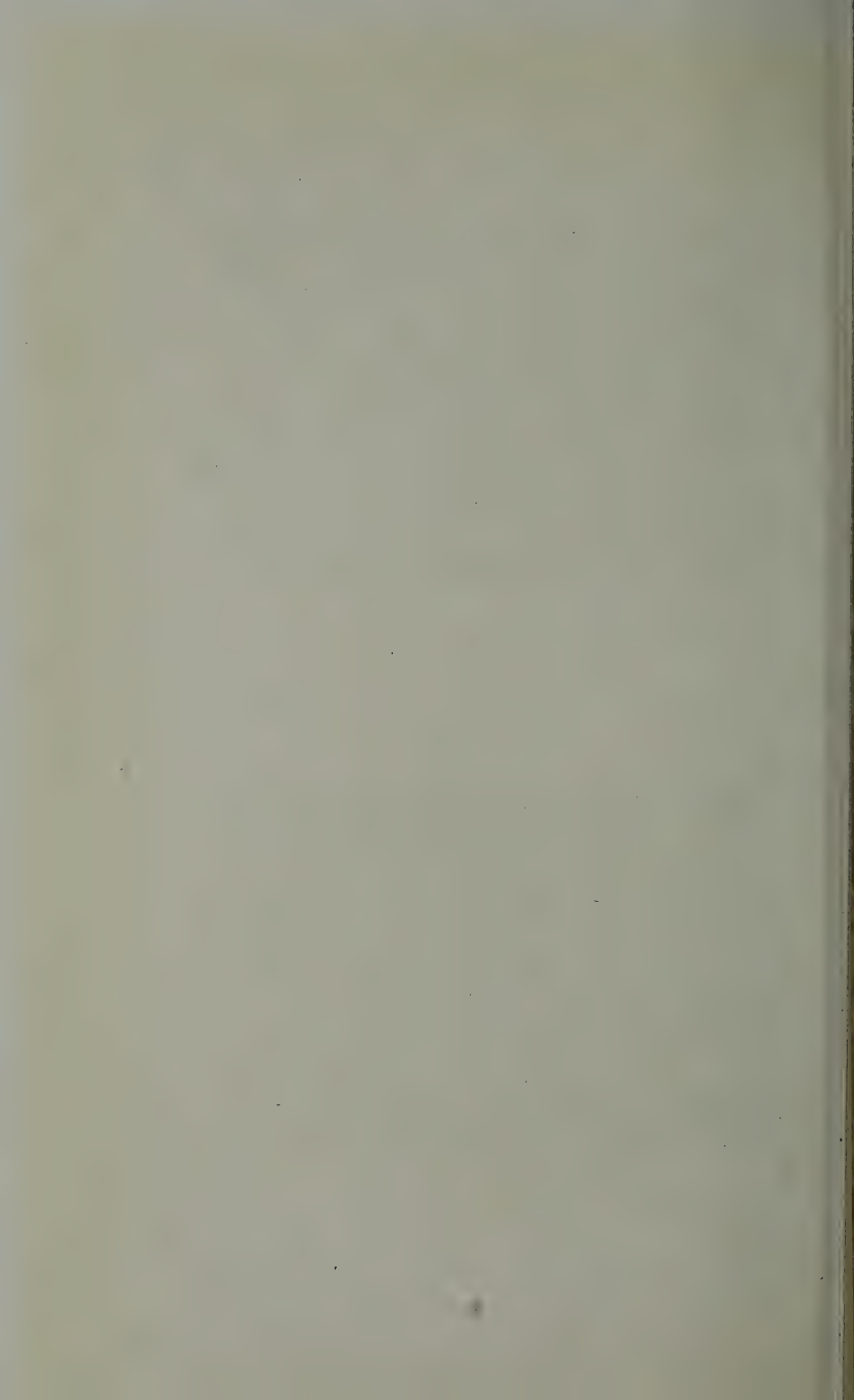


FIG. 89.—Hard Rolled.  $\times 50$  d.





MICRO-STRUCTURE OF BRASS.

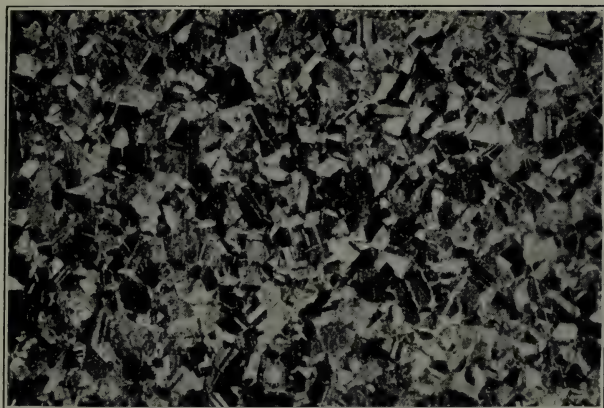


FIG. 90.—Annealed at 600° C.     $\times$  50 d.

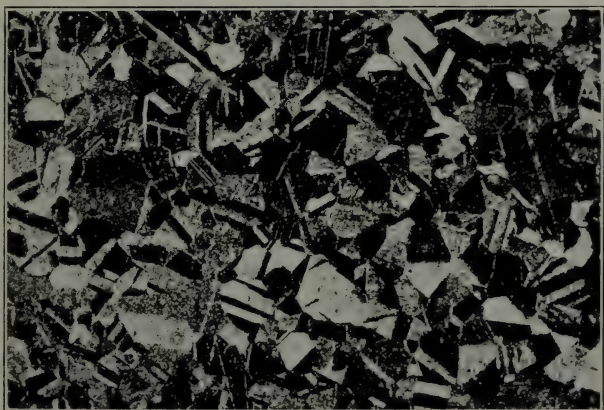
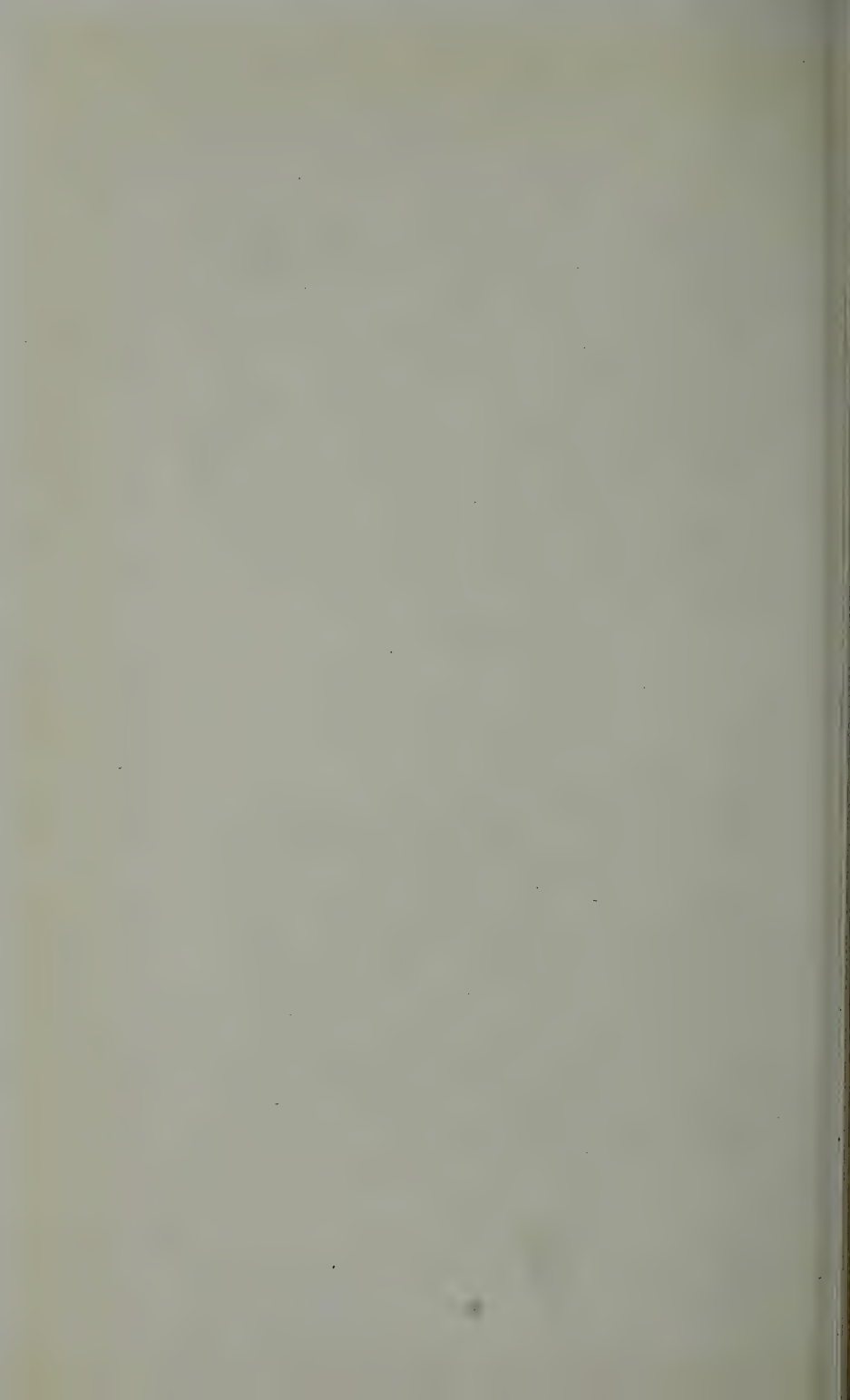


FIG. 91.—Annealed at 700° C.     $\times$  50 d.



MICRO-STRUCTURE OF BRASS.

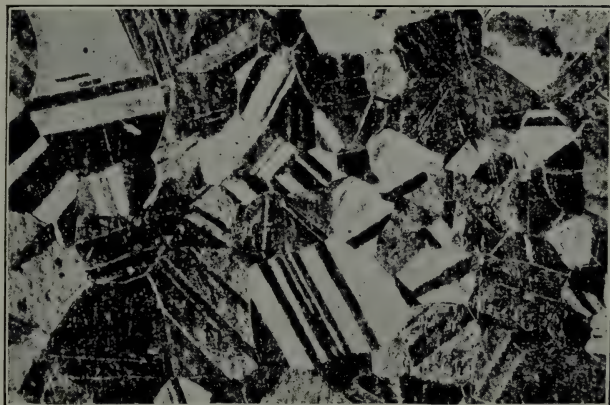
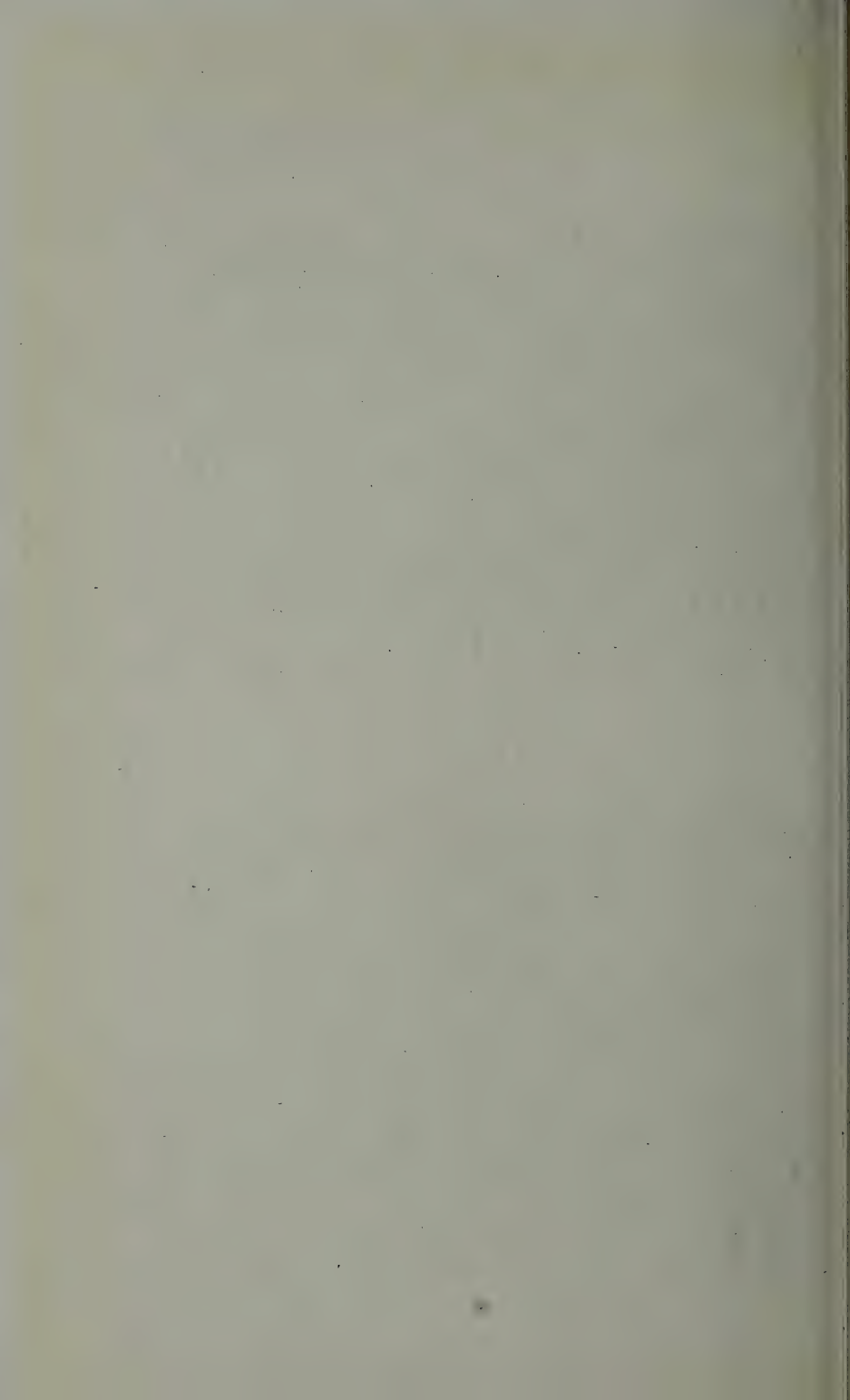


FIG. 92.—Annealed at 800° C.     $\times$  50 d.



FIG. 93.—Annealed at 900° C.     $\times$  50 d.





MICRO-STRUCTURE OF ALUMINIUM BRONZE.

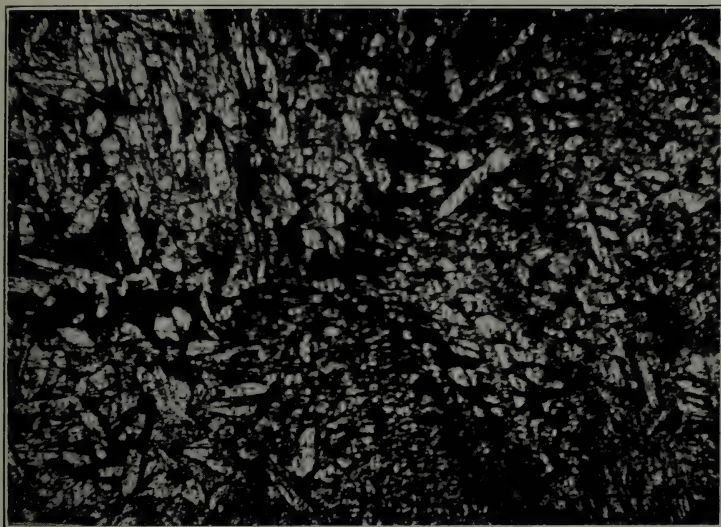


FIG. 94.—Cast in Sand.  $\times 100$  d

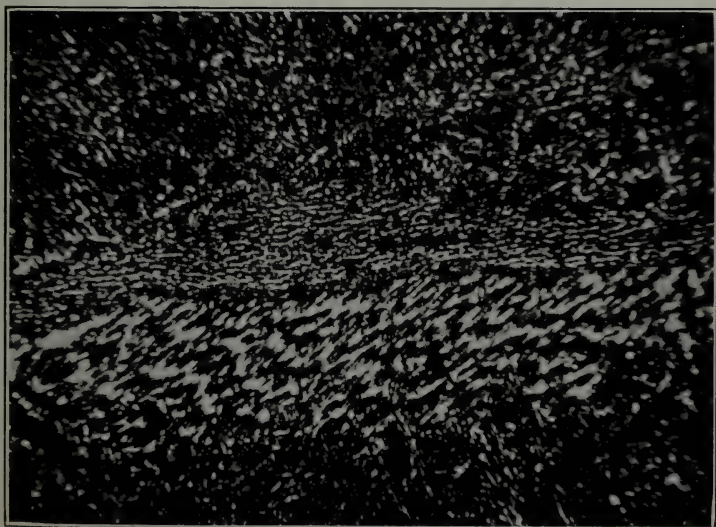


FIG. 95.—Cast in Chill.  $\times 100$  d.



MICRO-STRUCTURE OF ALUMINIUM BRONZE.

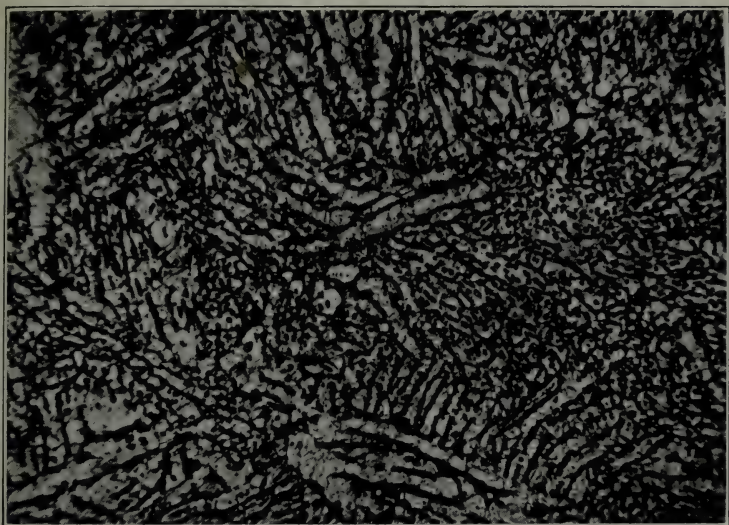


FIG. 96.—Forged.  $\times 100$  d.

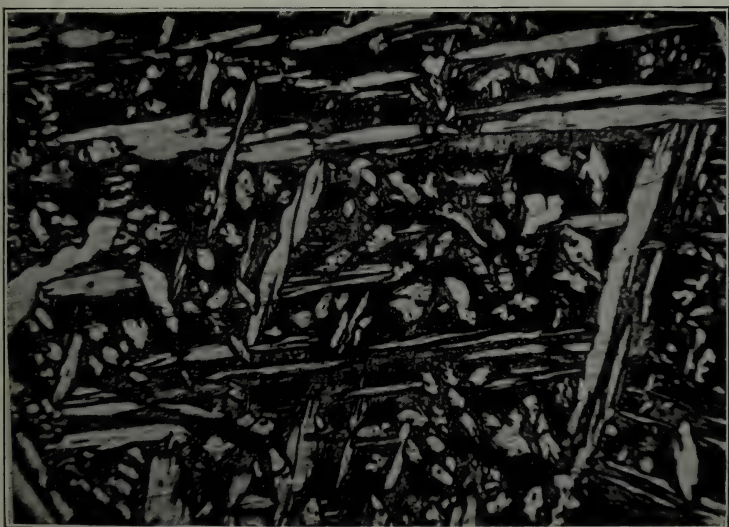


FIG. 97.—Annealed.  $\times 100$  d.

341  
- 377

06



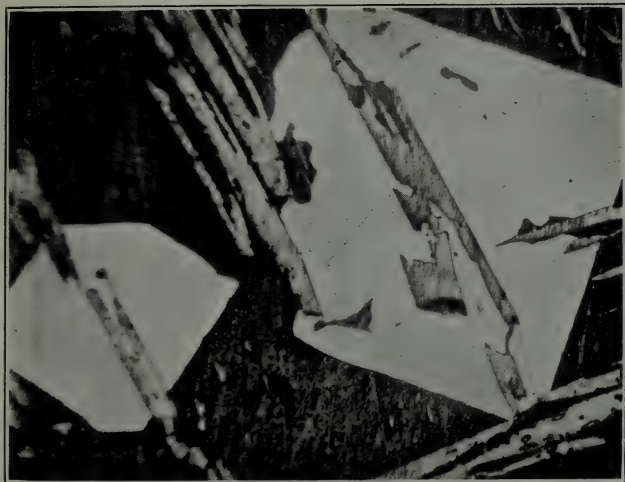


FIG. 98.—Sn-Sb-Cu Alloy.  $\times 100$  d.

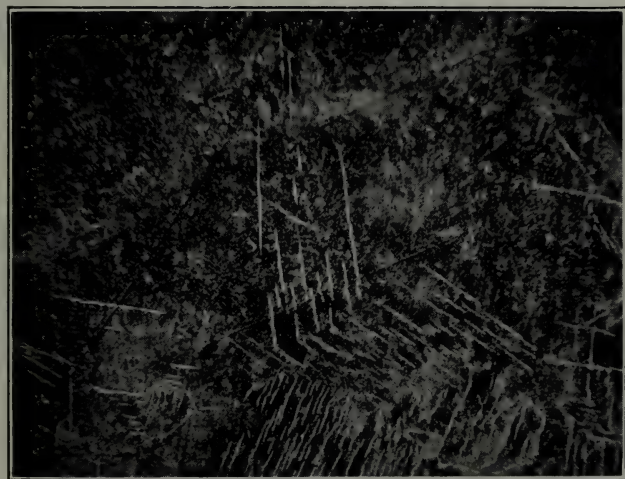


FIG. 99.—Cemented Carbon Steel.  $\times 100$  d.



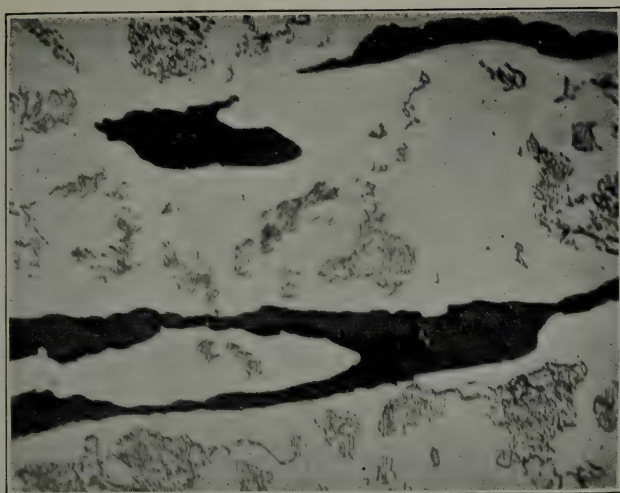


FIG. 100. —Slag Patches in Steel.  $\times 1000$  d.

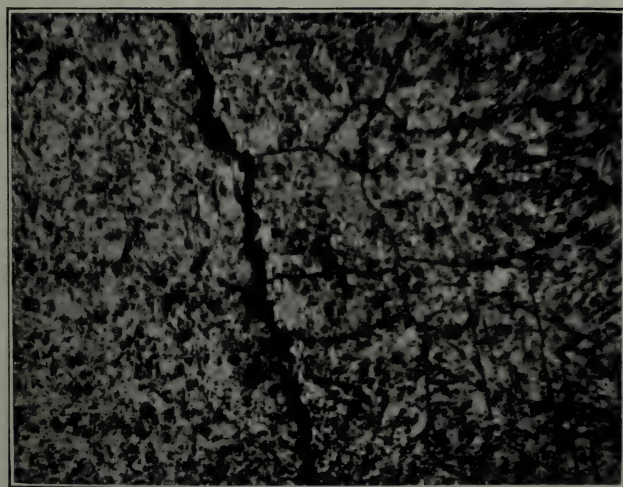


FIG. 101. ---Quenching Crack in Steel.  $\times 100$  d.

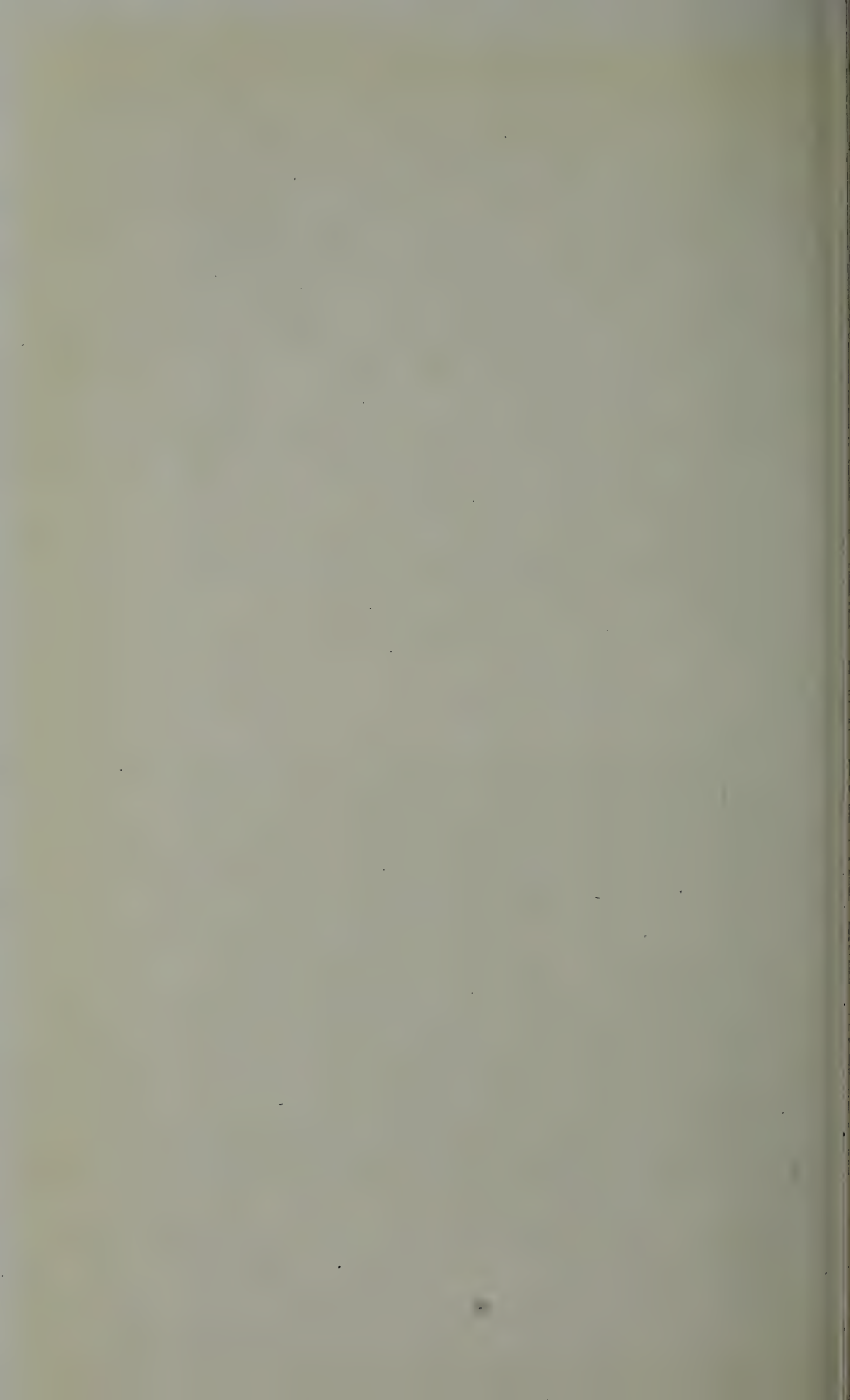






FIG. 102. — Crystals of Ferrite.

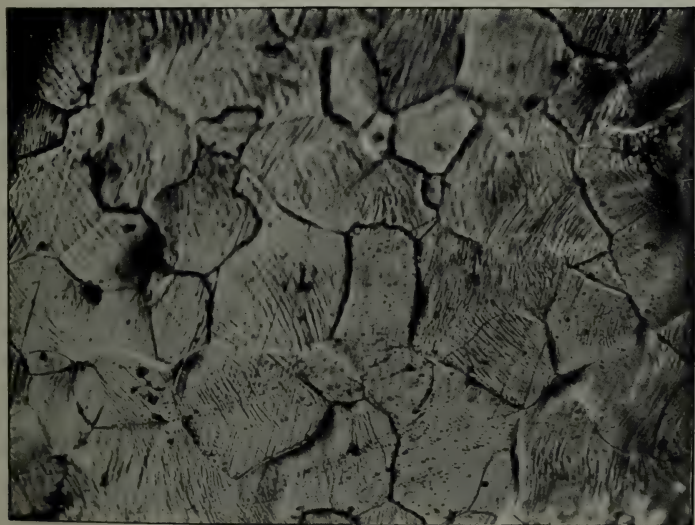


FIG. 103. — Slip-Bands in Ferrite Crystals.



the latter being illustrated in fig. 101, which shows a quenching crack in high carbon steel.

e. The detection of small quantities of impurities in metals which form eutectics around the grains of metal.

f. The effect of various stresses on structure, as illustrated in figs. 102 and 103, which show the formation of slip-bands in a piece of sheet iron, the bands having been formed by tensile deformation. These two photo-micrographs are taken from Mr Rosenhain's<sup>1</sup> paper on "Deformation and Fracture in Iron and Steel."

**Preparation of Photo-micrographs of Metals and Alloys.**—In order to obtain a successful photo-micrograph of a piece of metal or alloy, great care has to be taken in the preparation of the specimen by polishing and etching or otherwise developing the structure. In cases where large pieces are submitted for examination and report, such as steel rails, etc., it is well to polish a large section, etch this, and examine by means of a good lens or low-power microscope, in order to discover the portion most likely to yield useful results on thorough examination; in this manner the seat of the trouble is often quickly located. When it is decided which portion is to be examined, this is cut out by means of a hack saw, either a hand saw or an automatic power-driven saw being used. In the case of very hard specimens it is often necessary to break off a small portion by means of a sledge hammer, and to grind down the faces on an emery-wheel. In the case of very soft metals and alloys which are most difficult to polish, they are often cast on sheets of glass or mica, precautions being taken to prevent the formation of blowholes, the smooth surfaces thus obtained being suitably etched and then examined. In all cases it is far easier to get a good polish on hard than on soft materials. In ordinary cases, after cutting off the specimen, it is best to smooth the surfaces with files and roughly polish on emery cloth.

After this preparation, the polishing may be continued by one of several methods; for example, by the use of graded French emery papers mounted on revolving discs, the most usual grades being numbered respectively 0, 00, 000, and 0000; several types of electrically-driven machines have been devised for this purpose, and the papers are either attached to wooden discs by means of drawing-pins or mounted on iron discs by means of some adhesive such as seccotine.

Prof. H. Le Chatelier has devised a method of polishing by means of classified alumina powders, the details for the preparation of which are as follows:—Ammonium alum is calcined for a considerable time in a muffle in order to obtain alumina, and this is crushed and classified into a series of powders of varying degrees of fineness by means of a washing process.

The alumina is first treated with a 0.1 per cent. solution of nitric

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1906, No. 2, p. 189.

acid, one litre being used for every 10 grammes of powder, in order to dissolve out any salts of lime or other soluble compounds present. The mixture is then stirred occasionally for several hours and is allowed to settle, which it will do rapidly. It is then washed several times with water by decantation until it no longer settles rapidly, but remains in suspension for a considerable time. The operation of levigation now takes place, and this is facilitated by the addition of 2 c.c. of ammonium hydrate to each litre of water; this assists the finest particles to remain in suspension. Decantation is now resorted to at intervals of 15 minutes, 1 hour, 4 hours, 24 hours, and 8 days. The first deposit contains all the coarse particles unsuitable for polishing, the other four constituting an excellent series of polishing powders. Instead of waiting eight days for the last and finest deposit to settle, it may be thrown down quickly by neutralising the ammonia present with acetic acid, when the whole of the particles will be deposited in a few hours. The powders thus prepared are generally used on broadcloth mounted on revolving discs, and, for convenience in use, are often made into a paste kept in collapsible tubes, similar to those commonly used for oil paints. In order to prepare these pastes, the powders, obtained as above, are mixed with thin shavings of Castile soap, melted on a water bath, stirred thoroughly, and when the mass begins to thicken it is poured into the collapsible tubes. Other substances suitable for the preparation of polishing powders are chromic oxide, prepared by the ignition of ammonium bichromate, and ferric oxide, prepared by the ignition of oxalate of iron or by suitably washing the best jewellers' rouge. Other materials found useful in the preparation of various alloys are washed emery, tin oxide, diamantine powder, and globe polish, the latter being very suitable for brasses, bronzes, etc. The nature of the mount used for polishing has a considerable effect on the polished surface; for obtaining a perfectly smooth surface, a hard support such as glass is necessary, whereas, should relief polishing be desired, in which case the softer constituents are worn away, a soft support is necessary, such as a piece of rubber. For relief polishing, however, a rouge wheel is generally used, washed rouge being applied in the wet state on a revolving cloth-covered disc.

The amount of care and time devoted to the polishing operation will depend on the nature of the material, amount of etching possible, magnification required, etc. When unetched or heat-tinted specimens have to be photographed, very great care is necessary in order to eliminate all scratches.

In most cases, after the specimen has been suitably polished, the structure is developed, generally by one of the following methods:—

1. Simple attack by some solvent, such as nitric acid, sulphuric acid, hydrochloric acid, iodine solution, potassium cyanide,



ammonia, sodium hydrate, etc. Such a method may dissolve one component quicker than another; it may simply eat away the joints between adjacent grains or crystals, or it may colour one constituent differently to another and thus show up the structure.

2. Weyl's method consists of submitting the specimen to the action of a solvent under the influence of a feeble electric current. Charpy uses as poles the alloy under examination, and either platinum or an alloy very similar in composition to the specimen.

3. *Heat-tinting*.—In some cases the different constituents of an alloy may be differently tinted or coloured by gently heating the polished surface in air, the more oxidisable constituents being coloured by oxide tints. This method has been largely used by Stead, who has devised a special form of apparatus for heat-tinting under the microscope by means of an electric current. Some alloys, however, contain fusible constituents which melt before oxidation takes place properly; these may generally be tinted by slight heating in an atmosphere containing small quantities of bromine, iodine, or sulphuretted hydrogen.

4. Relief polishing, in which case the specimens are polished on a soft ground, such as cloth or leather, which causes the softer constituents to be worn away rapidly, leaving the harder constituents in relief.

5. *Polish Attack*.—This consists of finishing the polishing on a piece of wet parchment supported on a strip of wood and moistened with a 2 per cent. solution of ammonium nitrate, with which freshly precipitated calcium sulphate is used to assist the polishing.

*Mounting the Specimens*.—The specimens thus prepared for examination may be mounted on glass slips, or a mechanical or magnetic holder may be used. For temporary mounting, plasticine is best, a suitably sized true ring being used to mount the specimen absolutely flat. Hard canada balsam and lathe wax are also often used.

### The Microscope and its Accessories.

Although quite possible to obtain very creditable photo-micrographs with simple apparatus, such as a microscope fitted with an adjustable camera placed on a perfectly steady support and illuminated by an incandescent gas-light or an acetylene lamp, yet for systematic research work or for the production of high-power photographs a well-appointed optical bench, fitted with a good heavy microscope stand, and a separately mounted horizontal camera, such as the Zeiss apparatus shown in fig. 104, is greatly to be preferred. Such an equipment should have at one end an arc lamp, A (20 or 30 ampères), fitted with an automatic feed arrangement to minimise the amount of adjustment required to keep the light central; after this should be placed a double

meniscus lens, B, to obtain parallel rays of light, followed by a cooling chamber, C, to absorb the heat and keep the microscope objectives and specimens cool. Next on the bench is placed a plano-convex lens, D, to produce convergent rays condensed on the specimen under examination. This condenser should be "aplanatic," that is, corrected for aberration, which is a deviation of the rays of light when refracted by a lens, by which they are prevented from uniting in one point. In position, this lens should be so adjusted as to give a well-focussed image of the

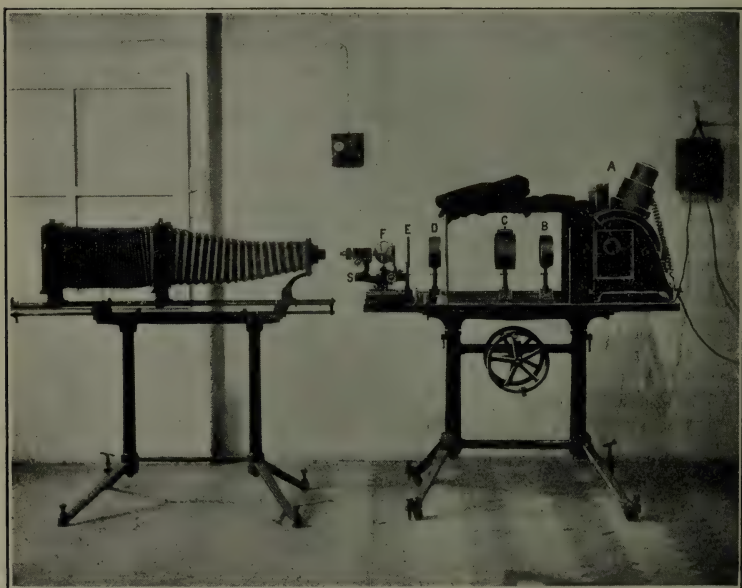


FIG. 104.—Microscopic Plant. A, lamp; B, double meniscus lens; C, cooling-chamber; D, plano-convex lens; E, iris diaphragm; F, mirror; S, stand.

crater of the arc-lamp on the window of the vertical illuminator. An iris diaphragm, E, is next placed on the bench, which should be arranged to give a very gradual variation of aperture; this is useful for exactly centring the light by closing down, and when in use must be adjusted so as to just illuminate the visual field. It is an advantage to use a green glass screen, as it renders the light monochromatic, cutting out the red rays, and increasing the contrast given by the specimen under observation.

For diverting the rays of light thus obtained on to the specimen a mirror, F, is required, and, when used in connection with the vertical illuminator, should be so placed as to give perfectly

horizontal rays, exactly at right angles to the main source of light.

There are several methods used for throwing the light on to the specimen, and the method will depend on whether "oblique" or "vertical" illumination is required, as the results obtained are quite different in the two cases: for example, if a perfectly flat surface be examined by oblique illumination, no rays will be reflected into the microscope, and such a surface will appear quite black; if, however, one constituent of the specimen be in relief, as the light falls upon one side of the projecting portion it will be reflected back into the microscope and will appear brilliantly illuminated, leaving the other side in shade.

For examination with low powers, the Sorby-Beck reflector is a useful type of illuminator, and by its use either oblique or vertical illumination may be obtained.

The construction of this illuminator is shown in fig. 105. It consists of a parabolic reflector, to which is attached a small

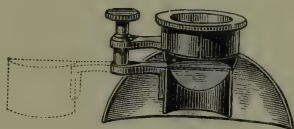


FIG. 105.—The Sorby-Beck Reflector.

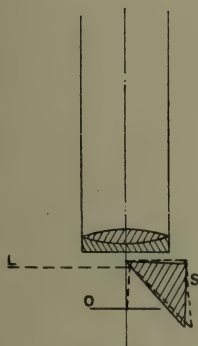


FIG. 106.

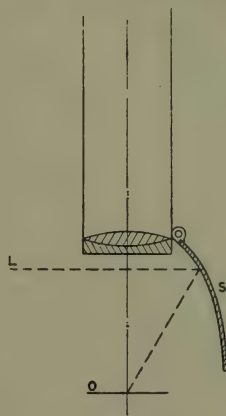


FIG. 107.

mirror with a face at an angle of  $45^\circ$ , which can be turned away from or under the object-glass by means of the milled head. When oblique illumination is required, the mirror is thrown outside into the position shown by the dotted lines, and the specimen is examined by light reflected from the silvered parabola. When direct illumination is required, however, the little mirror is turned back into the position shown in fig. 106, so that it partly eclipses the object-glass, but leaves room for the horizontal rays, L, reflected from the mirror on to the object, to be reflected

back from its surface into the microscope. In the case of oblique illumination, the horizontal rays of light, L (fig. 107), falling on to the parabola, are reflected at various angles upon the object below, and show up any of the constituents in relief. When vertical illumination is required for low-power work, it is not convenient to use the usual types of illuminator, as an insufficiently large field is illuminated, but a simple arrangement, suggested by Stead,<sup>1</sup> is more convenient for this purpose.

This arrangement is shown in fig. 108, and consists of a plain glass, G, placed at an angle of  $45^\circ$  between the specimen and the objective. The horizontal rays of light are partly reflected down on to the specimen, and then back from the object through the glass into the microscope. For high-power work direct illumina-

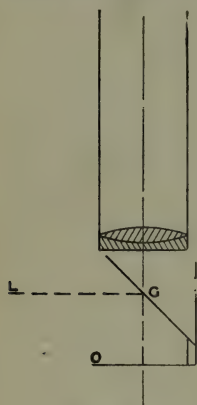


FIG. 108.



Beck's Illuminator.



FIG. 109.—Reflector.

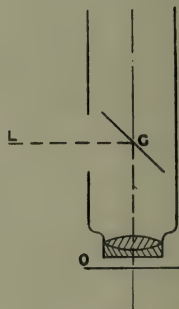


FIG. 110.

tion is always used, and Beck's illuminator is a useful form. It is exactly similar in principle to that just described, and consists of a metal collar or tube (fig. 109), in which is fixed on a pivot a cover-glass which acts as a reflector, and which can be rotated to any angle by the milled head shown, light being admitted to the reflector through an opening, A. The collar is screwed into the microscope tube, and the objective is then screwed on to the bottom of the collar, so that the reflector is in the tube of the microscope.

The reflector is turned to an angle of  $45^\circ$ , and the rays of light, L (fig. 110), admitted through the opening, A, fall upon the reflector, G, and are partly reflected down upon the object, and then up from its surface through the objective and reflector to the eyepiece.

Many workers now use a total reflecting right-angled prism

<sup>1</sup> "Practical Metallography," *Proceed. Cleveland Inst. of Engineers*, Feb. 26, 1900.



instead of the cover-glass reflector, as much better illumination of the field can thus be obtained. Figs. 111 and 112 show the form as supplied by Zeiss. In this case the rays of light, *L*, enter through a lateral opening in the mount of the apparatus, strike the hypotenuse surface of the reflecting prism, which covers one half of the aperture of the objective, and are thence totally reflected through the objective and concentrated upon the object, the image being produced solely through the open half of the objective. The diaphragms supplied for insertion in the vertical illuminator serve for two purposes:—

1. To prevent internal reflections of the mounts inside.

2. To cut off the very centre of the dioptric beam, known as the axial ray.

**Objectives and Eyepieces.** — Eyepieces should never be used with projection objectives or planar objectives.

The projection objectives usually used are listed as projecting aplanates, 35 mm. and 70 mm. in focal length.

For magnifications of about 50 diameters and for objects with considerable depth a 35 mm. planar objective is most useful; and if greater magnification is required, this is obtained by increasing the length of the camera. When using lenses with high focal length, the ordinary tube of the microscope is removed and a wider one inserted, to prevent the cutting out of some of the field.

For objects not possessing considerable depth long focus is not necessary, and a 16 mm. objective, together with a projecting eyepiece, either No. 2 or No. 4, is most useful.

For high magnifications, such as 1000 diameters, a 2 mm. oil immersion objective used in conjunction with a No. 4 eyepiece will be found satisfactory.

In order to calculate the magnification obtained in any case, the length of camera in millimetres is divided by the focal length of the objective, and multiplied by the magnifying power of the eyepiece.

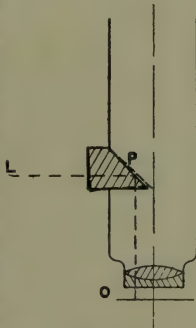


FIG. 111.

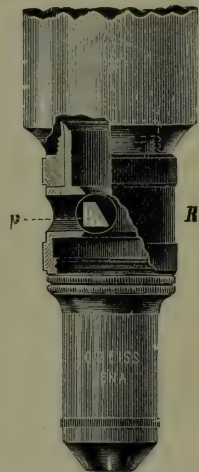


FIG. 112.

In order to calculate the visible field at any magnification, multiply the visible area of the objective by the magnification.

For oil-immersion lenses slightly thickened cedar oil is used, as this has practically the same refractive index as the glass from which the objectives are made.

### The Solution Theory of Alloys.

Our knowledge on subjects relating to alloys has advanced considerably of late years, owing for the most part to the combination of research by pyrometric and microscopic methods.

The methods of pyrometric examination have been considered in the previous chapter. The study of the molecular changes taking place during the solidification and cooling of metallic alloys has been greatly simplified by the adaptation of the solution theory, based on the similarity between the mode of solidification in alloys and in saline solutions.

Guthrie was the first to discover that the mixture of salt and water which had the lowest freezing-point contained about 23·5 per cent. of sodium chloride, and he came to the conclusion that this mixture was a hydrate of sodium chloride.

This and all similar bodies separating from saline solutions were called cryohydrates, meaning literally cold hydrates, or hydrates which could exist in the solid state at low temperatures only.

These cryohydrates have since been proved to be mechanical mixtures, and their counterpart in alloys are known as eutectics, which means literally "well-melting alloys." By taking a series of salt solutions containing successive additional amounts of salt and obtaining the points at which these solutions freeze, we shall have the necessary data for the construction of a freezing-point curve, from which valuable information can be obtained. Fig. 113 is such a curve for salt and water, and shows that each addition of salt to water, up to 23·5 per cent., depresses the freezing-point from 0° C. to - 22° C., and also shows the existence of a freezing-point at - 22 C. for all the mixtures, corresponding to the solidification of the cryohydrates. On further additions of salt being made the primary freezing-point rises, and in this case indicates the freezing out of salt, whereas below 23·5 per cent. of salt the primary freezing-point indicated the freezing out of pure water.

The maximum amount of salt soluble in water between 0° and 100° C. is just under 40 per cent., and fig. 113 is limited to this amount.

In freezing-point curves, the abscissæ represent composition and the ordinates represent the temperatures, and by following on the curves a substance of given composition we can ascertain the temperature at which freezing commences and at which solidifica-

tion is completed. Taking an example from the freezing-point curve of salt and water, fig. 113, suppose a solution containing 90 per cent. of water and 10 per cent. of salt be taken and placed in a cooling medium, when it reaches its freezing-point on the line ME ice will form, and there will be a retardation in the rate of cooling, denoting an evolution of latent heat; by this separation of ice the remaining solution becomes richer in salt, its freezing-point is lowered, and no further separation of

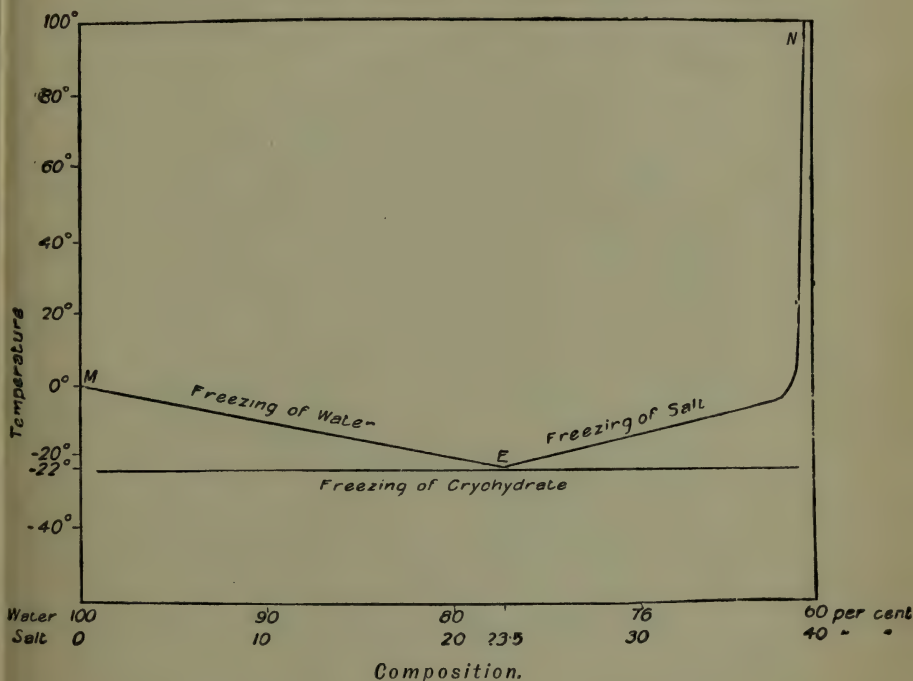


FIG. 113.—Freezing Curve of Solution of Common Salt.

ice will take place until its temperature is further lowered, when fresh formations of ice will take place along the line ME; when, however, a temperature of  $-22^{\circ}\text{C}$ . is reached no further selective action will take place, and the remaining liquid portion, which will contain 23.5 per cent. of salt, will solidify as a whole.

Supposing we now take a solution containing 30 per cent. of salt: on cooling we first get a retardation at a point on the line EN, and during this retardation solid salt will separate out, because the whole bulk of solution contains more salt than the cryohydrate ratio, 23.5 per cent.; as the temperature is lowered

from the commencement of freezing, more and more salt will crystallise out, leaving the liquid poorer and poorer in salt, and therefore richer in water, until again a temperature of  $-22^{\circ}\text{C}$ . is reached, when the still liquid portion will have the composition corresponding to the cryohydrate, and will solidify as a whole, no further selective freezing taking place.

If we now pass from saline solutions to fused alloys we find the same phenomena exhibited; for example, the copper-silver series of alloys, of which fig. 114 approximately represents the freezing-point curve (not the equilibrium curve), is very similar

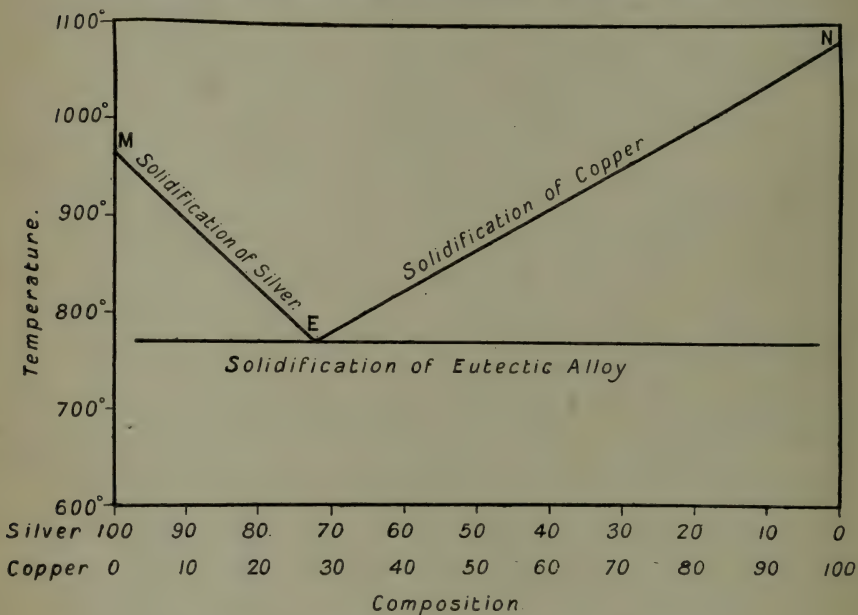


FIG. 114.—Freezing Curve of Copper-Silver Alloys.

to the salt-and-water curve given above. If we take an alloy containing 85 per cent. of silver and 15 per cent. of copper and cool down from a temperature of  $1000^{\circ}\text{C}$ . we shall again find a retardation at a temperature represented by a point on the line ME, where metallic silver, holding a certain amount of copper in solid solution, will first crystallise out; as the temperature is lowered from this point, silver will continue to crystallise out until a temperature of  $770^{\circ}$  is reached, at which temperature the portion remaining liquid will have become enriched in copper up to 28 per cent., and will solidify at this constant temperature; this is indicated at the point E on the diagram, and consists of



the eutectic alloy, which corresponds to the cryohydrate in the case of saline solutions.

The value of the combination of microscopic and pyrometric methods of examination will be evident on examination of fig. 115, which is a micro-photograph<sup>1</sup> of a silver-copper alloy of the same composition as the one taken above, that is, 85 per cent. silver and 15 per cent. copper; a polished surface of this alloy has been heated in the air, by which the copper portion has been oxidised and has been photographed at a magnification of 600 diameters. The white portions consist of metallic silver which has solidified

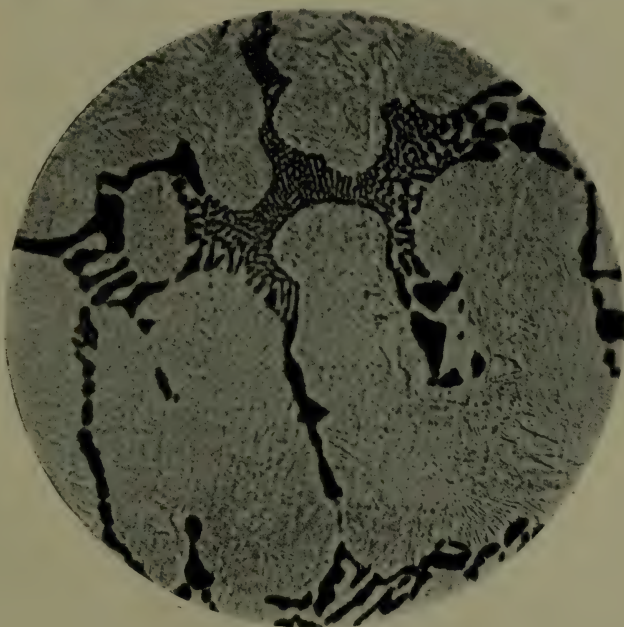


FIG. 115.

in advance of the eutectic, which can be seen in the darkened portions to consist of a conglomerate of copper and silver. If now an alloy of the eutectic composition be taken, it will be found that no retardation of temperature during cooling will take place until a temperature of  $770^{\circ}$  is reached, at which temperature the whole mass will solidify, forming a conglomerate of metallic silver and metallic copper. Fig. 116 is a micro-photograph of this alloy, prepared as above, and magnified 1000 diameters: it will be seen to be composed of alternate light and

<sup>1</sup> The three micro-photographs here reproduced are taken from Osmond and Stead's book.

dark portions, showing that it consists of alternate layers of silver and copper. If still another alloy of this series be taken and cooled from a high temperature—for example, one containing 65 per cent. of copper and 35 per cent. of silver—a retardation will be found at a point situated on the line E N, at which metallic copper will first crystallise out; and as the temperature is lowered, copper will continue to crystallise until  $770^{\circ}$  C. is reached, at which temperature the still liquid portion will have become enriched in silver up to 72 per cent.; and as this is the eutectic composition, the whole mass will now

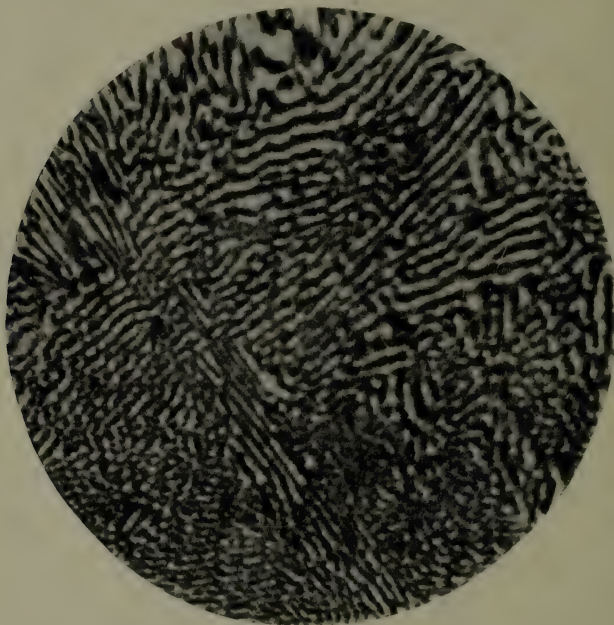


FIG. 116.

solidify into a conglomerate as before. Fig. 117 shows a photomicrograph of this alloy, magnified 600 diameters, in which the dark portions consist of the copper which has crystallised out along E N, and the lighter portions, which consist of solidified eutectic, will be seen to consist of a conglomerate of silver and copper as before.

The method of examination of alloy-series above indicated is now very largely used; but instead of merely noting the temperatures at which freezing commences and solidification is completed, every thermal change which takes place during the cooling of the alloy is noted, together with the duration of time these changes

occupy, and from the data thus obtained complete equilibrium curves are constructed. For obtaining perfect equilibrium many precautions are necessary, the most important being extremely slow cooling during the pyrometric observations.

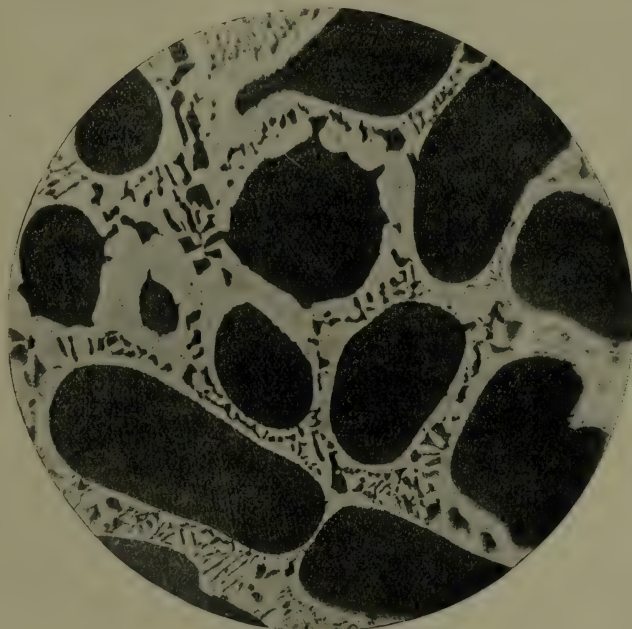


FIG. 117.

### THE CONSTITUTION OF METALLIC ALLOYS.

As a result of the work carried out by modern methods of research, it is now recognised that the constituents of metallic alloys may consist of one or more of the following :<sup>1</sup>—

1. Free metals in the pure state.
2. Solid solutions of one metal in another.
3. Definite chemical compounds of metals with metals.
4. Definite chemical compounds of metals with non-metals.
5. Eutectic mixtures.
6. Solid solutions of chemical compounds in excess of metal.
7. Allotropic modifications.

1. **Free metals in the pure state.**—These are metals which fall out of solution or crystallise out during the cooling down of

<sup>1</sup> See Lecture by Stead, Cleveland Inst. of Engineers, Dec. 10, 1900.



a molten alloy. They are found in the solid alloys as crystallites (skeleton crystals minus their crystal faces) or as perfectly formed crystals, and when present in these forms they have generally formed in a fluid matrix; if the pure metal, however, has a lower freezing-point than that part of the alloys which first crystallises, it is found between the crystals, filling up the interstices. In order to ascertain whether a constituent consists of pure metal, it is sometimes possible to dissolve away by some suitable solvent everything except the apparently pure metal, and then make an analysis of it.

This method is not always possible, however, as sometimes it is difficult to obtain a reagent which will attack the portion not required, and at the same time remain inactive on the metal it is sought to isolate. In this case it is advisable to use a synthetical method by melting the metal with varying minute quantities of the second element in question, and cooling the product extremely slowly. If, now, the resulting metal be cut, polished, etched, and examined by the microscope, and if minute traces of the second substance be detected, it may be assumed that the second substance does not form a solid solution with the metal, and therefore that the metal crystallises out in the pure state. This latter method of examination may also be used to determine exactly what amount of one metal will remain in solid solution in another. Examples of this constituent in alloys are found in the antimony-lead,<sup>1</sup> zinc-cadmium,<sup>2</sup> gold-lead,<sup>3</sup> aluminium-magnesium<sup>4</sup> series, etc.

**2. Solid Solutions of one Metal in another.**—A metallic solid solution is a solid substance containing the metals in such an intimate mixture that the highest power of the microscope cannot detect a second constituent on properly prepared sections.

Oswald defined solutions as being homogeneous mixtures which cannot be separated by mechanical means; but it must be remembered that many mixtures, *e.g.* eutectics, cannot be separated by mechanical means, although they may, by heat-tinting, etching, etc., be shown under the microscope to be mixtures, and therefore not homogeneous. Many mixtures of metals which form liquid solutions do not remain in solution when they solidify, and these are known as solidified or congealed solutions; it is very important to distinguish between these terms.

The definition generally accepted by metallographists is the following:—

A solid solution is a homogeneous mixture of two or more

<sup>1</sup> H. Gautier, Roland-Gosselin, *Bull. Soc. d'Encour. pour l'Ind. nationale*, 1896.

<sup>2</sup> H. Gautier, *Contribution à l'étude des Alliages*, 1901, p. 93.

<sup>3</sup> Vogel, *Zeitschr. f. anorg. Chemie*, 1905, xlv. p. 11.

<sup>4</sup> Grube, *ibid.*, 1905, xlv. p. 225.



substances in the solid state. Solid solutions of metals are also called isomorphous crystals or mixed crystals.

As a general rule, solid solutions crystallise in a form identical with or very closely approximating to that constituent which predominates.

In certain cases, solid solutions may be heterogeneous, especially when solidification and cooling has taken place at such a rate that diffusion has not had sufficient opportunity to render the whole mass homogeneous. For example, in the gold-silver series of alloys there is a tendency for the central portion of the crystals to differ in composition from their outside boundaries. In this case the first crystals to form are richer in gold than the initial alloy because the alloys richer in gold have higher freezing-points and, as crystallisation proceeds, the mother metal will become richer and richer in silver, and so the successive layers of crystal tend also to become richer in silver. Now if this solid alloy be kept at a temperature only a little below its freezing-point for a long time, diffusion will be assisted, and this will tend to make the solid mass a homogeneous solid solution. Solid solutions are found throughout the series of antimony-bismuth,<sup>1</sup> gold-silver,<sup>2</sup> gold-platinum,<sup>3</sup> iron-manganese<sup>4</sup> alloys, etc., and to a limited extent in the series of alloys lead-tin,<sup>5</sup> lead-silver,<sup>6</sup> silver-tin,<sup>7</sup> silver-copper,<sup>8</sup> etc.

**3. Definite Chemical Compounds of Metals with Metals or Intermetallic Compounds.**—Many of the metals combine chemically with one another in atomic proportions. The resulting compounds were called metallo-metallic salts by Guthrie. These chemical compounds are quite homogeneous, and are recognised by having certain characteristics different from those of the metals combined. The methods of determining the presence of chemical compounds in alloy series have recently been reviewed by Dr Desch,<sup>9</sup> and consist of the following:—

(a) *Thermal Method.*—By the examination of the results of observation of freezing-points and other thermal changes which take place during the cooling of many individual alloys belonging to a series. This method has been greatly improved by Prof. Tammann<sup>10</sup> in his method of *Thermal Analysis*, in which observations are made of the time occupied by each arrest on the

<sup>1</sup> Gautier, *Bull. de la Soc. d'Enc. p. l'Ind. nationale*, 1896.

<sup>2</sup> Roberts-Austen and Rose, *Chemical News*, lxxxvii., 1903, p. 2.

<sup>3</sup> Doerinkel, *Zeit. anorg. Chem.*, 1907, liv. p. 345.

<sup>4</sup> Levin und Tammann, *Zeit. für anorg. Chemie*, xlvii. p. 136.

<sup>5</sup> Rosenhain and Tucker, *Phil. Trans.*, 1908, ccix. A. p. 89.

<sup>6</sup> Heycock and Neville, *Phil. Trans.*, 1897, clxxxix. A. p. 137.

<sup>7</sup> *Ibid.*

<sup>8</sup> Roberts-Austen and Rose, *Proc. Roy. Soc.*, lxxvii., 1900, p. 105.

<sup>9</sup> *Journ. Inst. Metals*, 1909, i. p. 227.

<sup>10</sup> *Zeit. anorg. Chem.*, 1906, xlix. 113; 1907, lv. 289, etc.

cooling curve of an alloy. Such arrests may be due to the primary separation of crystals, to the solidification of the eutectic, to a reaction between solid crystals and the portion still molten, or to a transformation in the solid state. By plotting the times thus obtained against the composition, the composition corresponding to the maximum development of heat is obtained, and by extrapolation the point at which the arrest vanishes is also found more accurately than by direct observation.

This method is particularly useful in giving evidence for the existence of compounds. In the pure state these completely freeze at a definite temperature, and when these compounds form maxima on the freezing-point curve they are comparatively simple to detect, but sometimes no maxima are shown, and the compounds are the result of reactions between solid and liquid portions; in these cases evidence is obtained by observing the position at which the reactions on either side of the supposed compound reach zero, and when this position coincides with the maximum evolution of heat due to the formation of the compound, then the composition of this compound can be obtained.

(b) *Microscopic Method*.—This is chiefly used as a control on the thermal analysis. Compounds should show a perfectly homogeneous structure, and the addition of small quantities of either of the component metals should give rise to a new constituent. In some cases, however, it is difficult to differentiate between compounds and solid solutions, especially when perfect equilibrium is attained.

(c) *Electro-motive Force Method*.—The measurement of the difference of potential between an alloy and one of its component metals is often of great value in determining the presence of compounds: it is very important, however, to obtain exact conditions of work before the results can be relied upon. Puschin<sup>1</sup> has shown that the most regular results are obtained when a solution of a salt of the less electro-positive metal is used as the electrolyte, and the difference of potential between that metal and the alloy is determined. If curves be plotted for composition and E.M.F., the form of the curve will be found to vary according to the nature of the series of alloys under examination.

In a series in which neither compounds nor solid solutions are formed, such as the gold-thallium series, the constant potential of thallium should be exhibited throughout, whereas in a series in which solid solutions are formed throughout, such as the antimony-bismuth series, a smooth curve is obtained in which the potential of the dissolved metal steadily falls with the increase of concentration of the second metal. On the other hand, when

<sup>1</sup> *J. Russ. Phys. Chem. Soc.*, 1907, xxxix. 13, 353, 528, 869.

compounds occur, the curve shows a sudden drop at the composition of the compound, as in the case of the silver-tellurium series which contains the compound  $\text{Ag}_2\text{Te}$ .

(d) *Chemical Examination of Residues*.—This method consists of attacking alloys of varying composition with reagents capable of extracting one or other of the components and analysing the residues. It is, however, liable to lead to inaccurate results; and before accepting these, the residue should remain unchanged in composition after repeated alternate treatment with two different reagents,<sup>1</sup> and should also be absolutely homogeneous.

(e) *Hardness*.—The hardness of a series of alloys may be determined by one of the methods described in Chapter II., and these figures, when plotted against composition, often give valuable results. Compounds are frequently harder than the constituent metals, but in a few cases are softer; for example, the compound  $\text{Cu}_2\text{Sb}$  is softer than antimony;<sup>2</sup> they give sharp maxima or minima on the curves. When solid solutions are formed throughout the series a smooth curve is obtained on plotting the results, this curve showing a maximum at an intermediate point between the metals, as in the case of the gold-silver series. The limit of solubility in any series is marked by a break in the curve; and when metals do not form solid solutions or compounds, that is, when they are eutectiferous throughout, the hardness is practically a linear function of the composition.

(f) *Electrical Conductivity*.—When a curve is plotted having as ordinates composition and electrical conductivity, the presence of compounds is indicated either as maxima or as minima; with series consisting of solid solutions a curve with a deep minimum is obtained, and with eutectiferous series a straight line. See Curves, etc., given in Chapter III.

Dr Desch has prepared the following tables to show the inter-metallic compounds which are well established, the pairs of metals which give no evidence of the formation of compounds, and also the doubtful cases.

<sup>1</sup> Guerther, *Metallurgie*, 1908, v. 184.

<sup>2</sup> Baikoff, *Bull. Soc. d'Encourag.*, 1903, civ. part 1, p. 626.

TABLE I.

The existence and formulæ of the following intermetallic compounds appear to be well established :—

Ag <sub>3</sub> Al, Ag <sub>2</sub> Al	Cu <sub>2</sub> Se
Ag <sub>3</sub> Hg <sub>4</sub> , and others	Cu <sub>2</sub> Te, Cu <sub>4</sub> Te <sub>3</sub>
Ag Mg, Ag Mg <sub>3</sub>	Cu <sub>2</sub> Zn, Cu Zn, Cu <sub>2</sub> Zn <sub>3</sub>
Ag <sub>2</sub> Pt	
Ag <sub>3</sub> Sb	Fe Ni <sub>2</sub>
Ag <sub>2</sub> Se	Fe <sub>3</sub> Sb <sub>2</sub> , Fe Sb <sub>2</sub>
Ag <sub>3</sub> Sn	Fe Zn <sub>3</sub> , and another
Ag <sub>2</sub> Te	
Ag <sub>3</sub> Zn <sub>2</sub> , Ag Zn, Ag <sub>2</sub> Zn <sub>3</sub> , Ag <sub>2</sub> Zn <sub>5</sub>	Hg <sub>9</sub> K, Hg <sub>8</sub> K <sub>2</sub> , Hg <sub>3</sub> K, Hg <sub>2</sub> K
Al <sub>2</sub> Au, Al Au, Al Au <sub>2</sub> , Al <sub>2</sub> Au <sub>5</sub> , Al Au <sub>4</sub>	Hg Li <sub>3</sub>
Al <sub>3</sub> Ca	Hg <sub>4</sub> Na, Hg <sub>2</sub> Na, Hg Na <sub>3</sub> and four others
Al <sub>5</sub> Co <sub>2</sub> , Al Co, and another	Hg <sub>2</sub> Tl
Al Cr <sub>3</sub>	
Al <sub>2</sub> Cu, Al Cu, Al Cu <sub>3</sub>	K Pb <sub>2</sub> , K Pb <sub>4</sub> , and another
Al <sub>3</sub> Fe	K Sn <sub>2</sub> , K Sn <sub>4</sub> , and two others
Al <sub>3</sub> Mg <sub>4</sub>	K <sub>2</sub> Tl, K Tl
Al <sub>2</sub> Ni, Al <sub>2</sub> Ni, Al Ni	
Al Sb	Mg <sub>2</sub> Ni, Mg Ni <sub>2</sub>
Al <sub>3</sub> Ti	Mg <sub>2</sub> Pb
As <sub>2</sub> Cd <sub>3</sub>	Mg <sub>3</sub> Sb <sub>2</sub>
As <sub>2</sub> Cu <sub>5</sub> , As Cu <sub>3</sub>	Mg <sub>2</sub> Sn
As <sub>2</sub> Fe <sub>3</sub> , As Fe <sub>2</sub> , and others	Mg <sub>3</sub> Tl <sub>3</sub> , Mg <sub>2</sub> Tl, Mg <sub>3</sub> Tl <sub>2</sub>
As Ni, As <sub>2</sub> Ni <sub>5</sub>	Mg Zn <sub>2</sub>
Au <sub>4</sub> Cd <sub>3</sub> , Au Cd <sub>3</sub>	Mn <sub>2</sub> Sb, Mn <sub>3</sub> Sb <sub>2</sub>
Au <sub>2</sub> Pb, Au Pb <sub>2</sub>	Mn <sub>4</sub> Sn, Mn <sub>2</sub> Sn, Mn Sn
Au Sb <sub>2</sub>	
Au Sn, Au Sn <sub>2</sub> , Au Sn <sub>4</sub>	Na <sub>4</sub> Pb, Na <sub>2</sub> Pb, Na Pb, Na <sub>2</sub> Pb <sub>5</sub>
Au Te <sub>2</sub>	Na <sub>3</sub> Sb, Na Sb
Au Zn, Au <sub>3</sub> Zn <sub>5</sub> , Au Zn <sub>8</sub>	Na Se, Na <sub>2</sub> Se <sub>5</sub> , Na Se <sub>2</sub> , Na Se <sub>3</sub>
	Na <sub>4</sub> Sn, Na <sub>2</sub> Sn, Na <sub>4</sub> Sn <sub>3</sub> , Na Sn, Na Sn <sub>2</sub>
Bi <sub>2</sub> K, Bi <sub>2</sub> K <sub>3</sub> , Bi K <sub>3</sub> , and another	Na <sub>3</sub> Tl, Na <sub>2</sub> Tl, Na Tl
Bi <sub>2</sub> Mg <sub>2</sub>	Ni <sub>4</sub> Sb, Ni <sub>5</sub> Sb <sub>2</sub> , Ni Sb, and another
Bi Na, Bi Na <sub>3</sub>	Ni <sub>3</sub> Sn <sub>2</sub> and others
Bi <sub>3</sub> Ni, Bi Ni	Ni Zn <sub>3</sub>
Ca Cd, Ca Cd <sub>3</sub> , and another	
Ca Pb <sub>3</sub>	Pb <sub>2</sub> Pd, Pb Pd, Pb Pd <sub>2</sub> , Pb Pd <sub>3</sub>
Ca Sn <sub>3</sub>	Pb Pt, and two others
Ca Tl <sub>3</sub> , and another	Pb Te
Ca <sub>2</sub> Zn <sub>3</sub> , Ca Zn <sub>4</sub> , Ca Zn, and another	Pb Tl <sub>2</sub>
Cd <sub>3</sub> Cu <sub>2</sub> , Cd Cu <sub>2</sub>	Pt <sub>3</sub> Sn, Pt Sn, Pt <sub>2</sub> Sn <sub>3</sub> , and another
Cd Mg	
Cd <sub>5</sub> Na, Cd <sub>2</sub> Na	Sb <sub>2</sub> Se <sub>3</sub>
Cd <sub>3</sub> Sb <sub>2</sub> , Cd Sb	Sb <sub>2</sub> Te <sub>3</sub>
Cd Sn <sub>4</sub>	Sb Tl <sub>3</sub>
Co Sb, Co Sb <sub>2</sub>	Sb Zn, Sb <sub>2</sub> Zn <sub>3</sub>
Co <sub>2</sub> Sn, Co Sn	Sn Te
Co Zn <sub>4</sub>	
Cr Sb, Cr Sb <sub>2</sub>	
Cu <sub>2</sub> Mg, Cu Mg <sub>2</sub>	Also two ternary compounds—
Cu <sub>3</sub> Sb, Cu <sub>2</sub> Sb	Cd HgK
Cu <sub>4</sub> Sn, Cu <sub>3</sub> Sn, and perhaps others	Hg <sub>2</sub> KNa



TABLE II.

The following pairs of metals do not give evidence of the formation of a compound under the conditions of the investigations:—

Ag-As	Au-Bi	Cd-Tl	Fe-Pb
Ag-Au	Au-Cu	Cd-Zn	Fe-Pt
Ag-Bi	Au-Fe	Co-Cr	Fe-Tl
Ag-Co	Au-Ni	Co-Cu	Fe-V
Ag-Cr	Au-Pd	Co-Fe	Hg-Pb
Ag-Cu	Au-Pt	Co-Ni	Hg-Sn
Ag-Fe	Au-Tl	Co-Pb	Hg-Zn
Ag-Mn		Co-Tl	
Ag-Ni	Bi-Cd	Cr-Cu	Mg-Na
Ag-Pb	Bi-Co	Cr-Ni	Mn-Ni
Ag-Pd	Bi-Fe	Cr-Pb	Mn-Pb
Ag-Tl	Bi-Hg	Cr-Sn	
Al-Bi	Bi-Mn	Cu-Fe	Ni-Pb
Al-Cd	Bi-Pb	Cu-Mn	Ni-Tl
Al-Na	Bi-Sb	Cu-Ni	Pb-Sb
Al-Pb	Bi-Zn	Cu-Pb	Pb-Sn
Al-Si		Cu-Pd	Pb-Zn
Al-Sn	Ca-Fe	Cu-Pt	
Al-Tl	Cd-Fe	Cu-Tl	Sn-Tl
Al-Zn	Cd-Hg		
As-Pb	Cd-Pb	Fe-Mn	Tl-Zn

TABLE III.

The following pairs of metals enter into combination, but the formulæ of the compounds formed have not yet been satisfactorily determined:—

Ag-Cd	Bi-Ca	Cr-Fe	Hg-Sr
Al-Hg	Bi-Cu	Cr-Si	
Al-Mn	Bi-Tl	Cu-Hg	K-Na
Al-Pt			K-Zn
Al-Th	Ca-Sb	Fe-Mo	Na-Zn
Al-Ti	Cd-Co	Fe-Sn	
Al-W	Cd-K	Fe-W	Sb-Sn
	Cd-Ni		Se-Sn
Ba-Hg	Co-Cr	Hg-Rb	Se-Tl

#### 4. Definite Chemical Compounds of Metals with Non-metals.

—In exactly the same manner that certain metals combine with one another to form intermetallic compounds which act as constituents in certain alloys, so also compounds are formed between some metals and non-metallic elements, and a few of these are most important constituents in certain classes of alloys. Undoubtedly the most important of these compounds is the carbide of iron,  $\text{Fe}_3\text{C}$ , on the amount and condition of which in carbon-steels most of the valuable properties of the steels depend. Phosphorus and silicon also form important compounds.

The following table gives a list of the most important com-

pounds of metals with non-metals which occur as definite constituents of alloys :—

Co <sub>2</sub> Si	Fe <sub>2</sub> P, Fe <sub>3</sub> P
Co <sub>3</sub> Si <sub>2</sub>	Fe <sub>2</sub> Si, Fe Si
Co Si	
Co Si <sub>2</sub>	Mg <sub>2</sub> Si
Co Si <sub>3</sub>	Mn <sub>2</sub> Si, Mn Si
	Mn <sub>5</sub> P <sub>2</sub> and another
Cu <sub>3</sub> P	
Cu <sub>3</sub> Si, and others	Ni <sub>3</sub> P, Ni <sub>5</sub> P <sub>2</sub> , Ni <sub>2</sub> P
Cu <sub>2</sub> O	Ni <sub>3</sub> Si, Ni <sub>2</sub> Si, Ni <sub>3</sub> Si <sub>2</sub> , Ni Si,
	Ni <sub>2</sub> Si <sub>3</sub>
Fe <sub>3</sub> C	
Fe O	Sn <sub>3</sub> P <sub>2</sub>

5. **Eutectic Mixtures.**—By this term is meant a eutectic after solidification and separation into its constituent parts which remain in micro-juxtaposition in the alloy, thus forming a constituent. The term *eutectic* was first used by Guthrie in 1875 to indicate solidified mother liquor. A eutectic is that alloy of a series or portion of a series which has the *lowest melting-point*.

It is often advisable to prepare the eutectics in as pure a state as possible in order to carry out the various methods of investigation on them. The following are among the methods which have been devised for this purpose :—

(a) *Guthrie's Method.*—In this method the metals under examination were melted together; then the metal which was in excess over the eutectic ratio was allowed to crystallise out, and when the greater part had become solid, the residual alloy which still remained fluid was poured off and allowed to set. This crude eutectic was remelted and allowed to partially solidify, and the mother metal again poured off. This treatment was repeated until the mother metal invariably yielded an alloy of the same composition.

(b) *Roberts-Austen's Method.*—In this case a steel cylinder fitted with two loose steel plungers is used. The alloy under examination is placed in the cylinder between the plungers and suitable pressure applied to these. The cylinder is heated up, and when the temperature at which the eutectic melts is reached, it will be forced out between the plungers and the cylinder. The eutectic alloy first obtained may be re-treated. The temperature at which the eutectic is obtained may be ascertained by the insertion of a thermo-couple.

(c) *Stead's Method* for small quantities of low melting-point alloys. A portion of the molten alloy is poured on to a sheet of asbestos, and when the mass has solidified to a thick paste, a second sheet of asbestos is placed on top, and a wooden roller is rolled over the surface. The eutectic runs as a fluid drop in front of the roller, and may thus be separated and re-treated if desired.

(d) *Synthetical Method.*—As a general rule, the best method

for making a quantity of pure eutectic is to first ascertain the correct composition by thermal and microscopical methods, and then make up the alloy to this composition.

The following is a list of the most important properties, etc., of a eutectic alloy:—

- (a) A single melting and solidifying point.
- (b) A melting and solidifying point lower than that of the mean of its constituents.
- (c) A composition which is constant and independent of the initial composition of the alloy.
- (d) A composition not necessarily in simple atomic proportions.
- (e) It must be the most fusible alloy in a given series or portion of a series, for some series of alloys have more than one eutectic.
- (d) It consists of a conglomerate of distinct particles of the components, mechanically mixed.
- (e) It may consist of two or more metals which do not unite chemically, or two solid solutions.
- (f) It may consist of a free metal or a solid solution, and a compound.
- (g) It may consist of two or more compounds.
- (h) It may be formed in the solid alloy, that is, at a temperature lower than that at which freezing is completed. The most important example of this is pearlite, which forms in the solid in carbon-steels, and is generally known by the term "eutectoid."
- (i) It may possibly consist of two eutectics, one formed during solidification, and the second after solidification is complete.

The exact microscopic structure of eutectics is found to vary in different alloy-series, and the following types may be considered as the most important.

*Curviplanar*, in which the constituents consist of curved plates in juxtaposition. Examples of this are found in the alloys of silver and copper, lead and tin, slowly cooled steels, etc.

*Honeycombed or Cellular*.—This is a very common eutectic structure, and is found in bismuth-tin, gold-lead, iron-phosphorus series, etc.

*Spherulitic*.—This is frequently met with, especially when the eutectics have been cooled down rapidly. The constituents commence to separate and solidify from nuclei, and grow from these; found in alloys of lead and antimony, lead and gold, etc.

*Geometric crystalline forms* are occasionally found in eutectics allowed to solidify very slowly; for example, the antimony-lead eutectic yields hexagonal prisms built up of alternate laminæ of lead and antimony; the gold-lead eutectic yields cuboidal forms.

The following series of alloys serve as examples in which eutectics are important constituents:—

Pb-Sb; Cd-Zn and AuTi, which contain eutectics practically throughout; Sn-Pb; Pb-Ag; Sn-Ag; Sn-Bi; Sn-Zn; Cu-Au; Cu-Ag; Al-Zn, etc., which contain eutectics only within certain



limits of composition; and Pb-Mg; Sn-Mg; Sn-Ni; Zn-Sb; Te-Bi; Na-Sn; Fe-Si; Au-Sn, etc., which yield two or more distinct eutectics, each one occurring within a certain range of composition only.

#### 6. Solid Solutions of Definite Compounds in excess of Metal.

—It has already been shown that chemical compounds form an important constituent of many series of alloys, and it will be readily understood that many of these compounds form solid solutions with excess of either or both of the elements of which they are composed, thus forming a new constituent. In a few cases the compound and each metal are completely soluble in each other, the best example of this being the magnesium-cadmium series; in other cases the compound and component metals are only partially soluble in each other, as in the copper-antimony series.

In commercial alloys the most important instances of solid solutions of compounds are found in the copper-tin and copper-zinc alloys, and very important solid solutions of compounds, containing a non-metal, are met with in the case of iron, in which, under suitable conditions, solid solutions may be formed with the compounds  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_3\text{P}$ , and  $\text{FeO}$ .

#### 7. Allotropic Modifications.

—It is recognised that many metals are capable of existing in two or more allotropic conditions, each modification being stable only within certain limits of temperature; this phenomenon is also exhibited in the alloys of these metals containing only a certain amount of a second metal, but in a less marked manner.

Certain definite compounds of metal also exhibit similar polymorphic changes. Any change in the nature of the structural constituents of solid alloys takes place with difficulty unless the material is cooled extremely slowly, and may be prevented almost entirely by rapid cooling in the neighbourhood of the transition temperature. The velocity of transformation varies considerably at different temperatures, being greater the higher the temperature, and the farther this temperature is removed from the transition point. Above the temperature of the transition point both these conditions act in the same direction, and the velocity of transformation is increased indefinitely as the temperature is raised. Below the transition point, however, these two conditions act in opposite directions, the velocity being decreased by lowering the temperature, but increased by withdrawing farther from the transition temperature; it will thus be seen that there must be a certain temperature at which the transformation will take place with a maximum velocity. Below this temperature the velocity of transformation decreases with comparative rapidity, and may possibly become zero, showing how it becomes possible to maintain certain metals in an unstable allotropic state at ordinary temperatures.



A simple illustration of allotropic change is found in the gold-thallium alloys;<sup>1</sup> pure thallium possesses a transition point at 225° C., and an arrest is found at this temperature in all the alloys containing primary precipitated thallium; in an equilibrium diagram this change appears as a straight horizontal line. Similar allotropic changes are found in many of the alloys containing nickel, cobalt, etc., corresponding to the temperature at which magnetic transformations take place. The allotropic changes which take place during the cooling of iron and iron-carbon alloys have already been mentioned. Rosenhain<sup>2</sup> has recently described a similar change in lead-tin alloys containing between 8 and 63 per cent. of tin; the change takes place at a constant temperature of 149° C. for the alloys containing above 18 per cent. of tin, and at lower temperatures for alloys of lower tin-content. This change involves the rejection of tin from the solid solution, the form stable at low temperatures possessing a smaller solubility for tin than the form stable above 149° C. As examples of similar changes taking place in metallic compounds, mention may be made of the compound  $\text{Na}_4\text{Sn}_3$  occurring in the sodium-tin series;<sup>3</sup> this compound changes with an increase of volume at a temperature below solidification. The compound  $\text{AuPb}_2$  also exhibits allotropic change after solidification, as do also the compounds  $\text{Co}_5\text{As}_2$ ,  $\text{Co}_2\text{As}$ ,  $\text{Co}_3\text{As}_2$ , besides many more.

**Classification of Binary Alloys.**—Undoubtedly the best method of classification for alloys of two metals is based on the type of equilibrium curve obtained. The subject is far too extensive for full treatment in this book, and will be given in outline only; for a fuller description the student is referred to Gulliver's *Metallic Alloys*. In the following groups, however, are included the most important types of freezing-point curves.

*Group I. Alloys.*—These are obtained by alloying any two metals which are completely mutually soluble in the liquid state, and completely insoluble in the solid state. In these alloys a eutectic is found at a certain composition, and intermediate alloys between the pure metals and the eutectic consist of two constituents, viz. crystals of the pure metal which happens to be in excess over the eutectic ratio, and the eutectic itself.

An example of this group of alloys is found in the lead-antimony series, the equilibrium diagram of which is given in fig. 118, after Roland Gosselin.<sup>4</sup> It will be seen that the eutectic point occurs with a composition of 13 per cent. of antimony and 87 per cent. of lead, and that the eutectic temperature is 228° C. All the alloys between pure lead and that one containing 13 per

<sup>1</sup> Levin, *Zeit. anorg. Chem.*, 1905, xlv. p. 31.

<sup>2</sup> *Phil. Trans.*, 1908, Series A, vol. ccix. pp. 89-122.

<sup>3</sup> Mathewson, *Zeit. anorg. Chem.*, 1905, xlv. p. 94.

<sup>4</sup> *Contribution à l'étude des Alliages*, 1901, p. 93.

cent. of antimony will commence to freeze at some temperature indicated on the line Pb.E., and at this temperature crystals of pure lead will be deposited; as the temperature falls, lead crystals will continue to be thrown out of solution until a temperature of  $228^{\circ}$  is reached, when the still liquid portion will contain 87 per cent. of lead, no matter what the initial composition of the alloy was, and this liquid portion of eutectic composition will solidify as a conglomerate of crystals of pure lead and pure antimony. If an alloy consisting of 13 per cent. of antimony be taken, no crystallisation will take place during cooling until the eutectic temperature  $228^{\circ}$  is reached, when the alloy will solidify as a whole at this definite temperature. Alloys containing more than 13 per cent. of antimony will resemble the alloys containing less than 13 per cent. of antimony in the mode of solidifying, except that the first crystals to fall

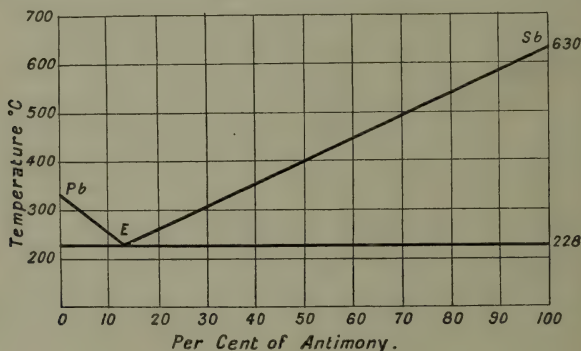


FIG. 118.

out of solution will consist of pure antimony instead of pure lead.

Thus all alloys between the eutectic composition E and pure antimony will commence to solidify at some temperature on the line E.Sb, and the crystals formed will consist of pure antimony; as the temperature falls, antimony will continue to be deposited until the portion remaining liquid contains only 13 per cent. of antimony; as before, this state of affairs will be reached at a temperature of  $228^{\circ}$ , at which temperature solidification will be completed. It should be remembered that the micro-structure of these alloys is closely connected with the deductions drawn from the freezing-point curve, and resembles the micro-structure of the silver-copper alloys (see page 223).

*Group II. Alloys.*—These are obtained by alloying any two metals which are completely mutually soluble in the liquid state and partially soluble in the solid state. In these alloys the general

form of the freezing-point curve resembles that of the Group I. curves, except that the eutectic line does not extend throughout the series. A eutectic is found at a certain composition as before, and in alloys of any other composition the excess metal crystallises out as a solid solution, the amount of the second metal held dissolved varying with the metals under consideration.

An example of this important group of alloys is found in the aluminium-zinc series, the equilibrium diagram of which is given in fig. 119, after Shepherd.<sup>1</sup> The conclusions drawn from this diagram, which are confirmed by microscopic analysis, are that above the line  $ZnEa$  the alloys consist of homogeneous fluids. In the region  $ZnEa$ , primary crystals of zinc holding a certain amount of aluminium in solution (the amount dissolved being indicated by line  $Zn a$ ) are in equilibrium with a still molten portion of the alloy; similarly, in the region  $Ea b$ , crystals of aluminium holding an amount of zinc, indicated by  $Al b$ , exist in equilibrium with a still molten portion of the alloy. At the temperature of the straight line  $aEb$ , the eutectic solidifies and is made up of two solid solutions, one having composition  $a$  and the other of composition  $b$ . In this series, alloys containing up to 4 per cent. and also those containing more than 45 per cent. of aluminium are homogeneous in structure, and only the alloys between these limits consist of two constituents. The fact that the lines  $ad$  and  $bc$  are not vertical indicates that the mutual solubility of these metals varies with the temperature; for example, solid aluminium at 200° is capable of holding in solid solution more zinc ( $fc$ ) than at a temperature of 300° C.

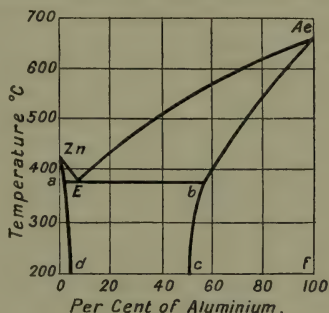


FIG. 119.

Group III. Alloys.—These are obtained by alloying any two metals which are completely soluble in each other, both in the liquid and in the solid state. When absolute equilibrium is attained in these alloys they possess a homogeneous structure, but in the ordinary course of freezing the first crystals to separate are invariably richer in that metal having the higher melting-point, and the last portions to crystallise are correspondingly richer in the metal with the lower melting-point. Distinct differences can generally be seen in the appearance of the individual crystals after polishing and etching, owing to the gradual variation in composition from the centre to the outside.

<sup>1</sup> *Journ. Phil. Chem.*, 1905, ix. p. 504.



As an example of this series of alloys, those of antimony-bismuth may be taken, the freezing-point curve of which is shown in fig. 120, after Gautier.<sup>1</sup> The full line BiASb indicates the temperature of the commencement of solidification, and the dotted line BiCSb indicates the temperature at which solidification is complete; this part of the diagram, however, has not yet been determined with accuracy. To illustrate the mode of procedure of the freezing in this case, suppose an alloy of 50 per cent. Sb and 50 per cent. Bi be cooled down from some temperature above 600°. The molten alloy will merely cool down until a temperature of 500° is reached (A), at which solidification will commence, the first crystals to be deposited being of composition B, that is, containing about 75 per cent. Sb. From 500° downwards crystallisation will proceed, the crystals being deposited becoming poorer and poorer in Sb, and correspondingly richer in Bi, until a temperature of about 400° is reached, when the

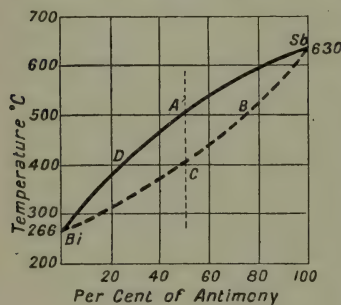


FIG. 120.

whole mass will be solid, the last portion to solidify having a composition D, or about 25 per cent. Sb.

By keeping the alloy at a temperature just below solidification for a long time diffusion is assisted, and continues until the whole mass is homogeneous in composition. To this group belong the series Au-Ag, Au-Pt, Mn-Fe, Ni-Co, Pd-Ag, Pd-Au, etc.

*Group IV. Alloys.*—These are obtained by alloying metals which form chemical compounds.

It will be readily seen that this group may be subdivided according to whether the compound or compounds are completely soluble, partially soluble, or completely insoluble in the other constituents of the alloy. As an example, the tin-magnesium series may be taken, the equilibrium diagram of which is given in fig. 121 after Grube. It will be noticed that at C a maximum point is obtained; this is found in the alloy containing 71 per cent. of tin, and corresponds to the compound  $\text{SnMg}_2$ , which has a freezing-point of 783°C.

If this type of diagram be divided vertically through C (the compound) two diagrams will be obtained, each similar to the diagrams given by Group I. Alloys, the compound taking the place of one of the pure metals. The composition of the various portions is clearly indicated on the diagram, both for temperatures at which crystallisation has commenced and for temperatures at which the alloys are completely solid.

<sup>1</sup> Bull. de la Soc. d'Enc. p. l'Ind. nationale, 1896.



For a complete consideration of the Phase Rule and its application to the study of alloys, which is of very great value, the student is referred to the books already mentioned, and to the original papers given in the following bibliography. The consideration of the equilibrium curves of the very important series

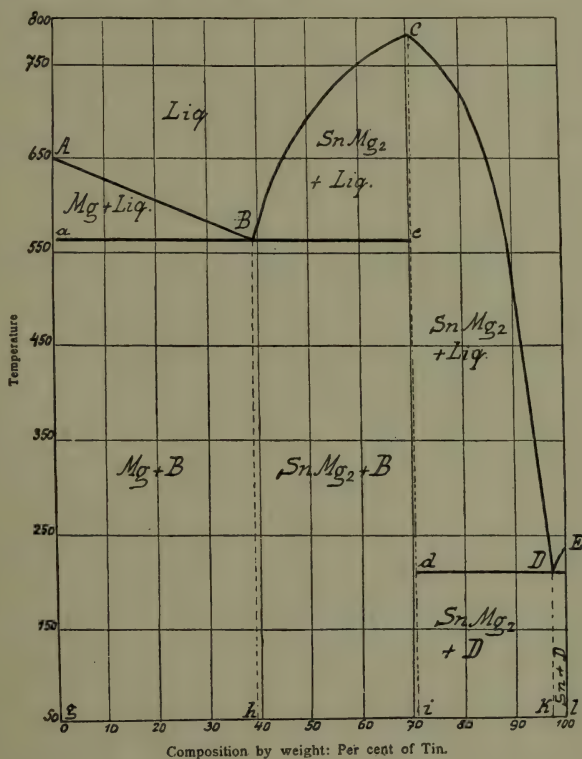


FIG. 121.—Group IV. Alloys.

of alloys copper-zinc, copper-tin, copper-aluminium, and iron-carbon is omitted, as being complex and beyond the scope of this work. These important classes of industrial alloys have received a large amount of attention from metallographists, and comprehensive accounts of their constitution and properties are fairly accessible.

## BIBLIOGRAPHY.

- H. C. Sorby.—*On a New Method of Illustrating the Structure of Various Kinds of Steel by Nature Printing* (Sheffield Literary and Philosophical Society, February 1864).
- H. C. Sorby.—*On the Microscopical Structure of Meteorites and Meteoric Iron* (Proceedings Royal Society, vol. xiii. p. 333, and British Assoc. Report, 1865, part i. p. 139).
- H. C. Sorby.—*On Microscopical Photographs of Various Kinds of Iron and Steel* (British Assoc. Report, 1864, part ii. p. 189).
- H. C. Sorby.—*On the Microscopical Structure of Iron and Steel* (Dr Lionel Beale's *How to Work with the Microscope*, 4th ed., 1868, pp. 181–183).
- A. Martens.—*Ueber die mikroskopische Untersuchung des Eisens* (Zeits. des Ver. Deutsch. Ing., vol. xxi. pp. 11, 295, and 481, Jan., May, and Nov. 1878; and vol. xxiv. p. 397, Aug. 1880).
- H. C. Sorby.—*Lecture delivered in Sheffield's Firth College*, read Oct. 20, 1882 (The Engineer, vol. liv. p. 308, Oct. 27, 1882).
- A. Martens.—*Ueber die mikroskopische Untersuchung des Eisens* (Verhandl. des Ver. zur Beförderung des Gewerbflusses, Sitzungsberichte, 1882, p. 233).
- J. C. Bayles.—*Microscopic Analysis of the Structure of Iron and Steel* (Trans. Am. Inst. Min. Eng., vol. xi. p. 261, 1883).
- O. Dolliak.—*Beiträge zur Mikroskopie der Metalle* (Mittheil. über Gegenstände des Artillerie- und Geniewesens, 1883, Heft 9, p. 467).
- A. Martens.—*Erläuterungen einer in der kön. Bergakademie zu Berlin befindlichen Sammlung von 120 Schläfen zur Darstellung des mikroskopischen Gefüges verschiedener Eisen- und Stahlsorten*, Berlin, 1884.
- F. Osmond et J. Werth.—*Structure Cellulaire de l'Acier Fondu* (Comptes Rendus, Acad. des Sciences, vol. c. p. 450, Feb. 16, 1885).
- F. Lynwood Garrison.—*The Microscopic Structure of Iron and Steel* (Trans. Am. Inst. Min. Eng., vol. xiv. p. 64, 1885).
- H. Wedding.—*The Properties of Malleable Iron, deduced from its Microscopic Structure* (Journal of the Iron and Steel Inst., 1885, p. 187).
- F. Osmond et J. Werth.—*Theorie Cellulaire des Propriétés de l'Acier* (Ann. des Mines, 8th series, vol. viii. p. 5, July to Aug. 1885).
- F. Lynwood Garrison.—*The Microscopic Structure of Cart-Wheel Iron* (Trans. Am. Inst. Min. Eng., vol. xiv. p. 913, 1886).
- H. C. Sorby.—*On the Application of very High Powers to the Study of the Microscopical Structure of Steel* (Journal of the Iron and Steel Inst., 1886, p. 140).
- H. Wedding.—*Die Mikrostruktur des gebrannten Eisens* (Stahl und Eisen, vol. vi. p. 633, Oct. 1886).
- H. Wedding.—*Die Mikrostruktur des Eisens* (Stahl und Eisen, vol. vii. p. 82, Feb. 1887).
- F. Lynwood Garrison.—*Microscopic Structure of Steel Rails* (Trans. Am. Inst. Min. Eng., vol. xv. p. 761, Feb. 1887).
- A. Martens.—*Ueber das Kleingefüge des schmiedbaren Eisens, besonders Stahls* (Stahl und Eisen, vol. vii. p. 235, Apr. 1887).
- H. C. Sorby.—*The Microscopical Structure of Iron and Steel* (Journal of the Iron and Steel Inst., 1887, p. 255).
- H. Schild.—*Die neuesten Forschungen auf dem Gebiete der mikroskopischen Untersuchung von Stahl und Eisen* (Stahl und Eisen, vol. viii. p. 90, Feb. 1888).
- H. Wedding.—*Zusammenhang zwischen der chemischen Zusammensetzung und dem Kleingefüge einerseits und der Leitungsgüte des Telegraphendrahtes andererseits* (Mittheil. aus den kön. technischen Versuchsanstalten, 1888, Ergänzungsheft i. p. 6).
- H. Wedding.—*Ueber Fortschritte in der Lichtabbildung des Kleingefüges von Eisen und die Herstellung von Schläfen* (Stahl und Eisen, vol. ix., Apr. 1889).

- A. Martens.—*Ueber die mikroskopische Untersuchung des Kleingefüges von Eisen* (Stahl und Eisen, vol. ix. p. 393, May 1889).
- F. Osmond.—*Le Fer et l'Acier* (Lumière Electrique, vol. xxxv. p. 265, Feb. 8, 1890).
- H. Wedding.—*Das Kleingefüge des Eisens. Mikroskopische Original-photographien mit Erläuterungen* (Berlin, 1891).
- Sir Fr. Abel.—*Presidential Address* (Journal of the Iron and Steel Inst., 1891, part i. p. 18).
- F. Osmond.—*Note on the Micro-structure of Steel* (Journal of the Iron and Steel Inst., 1891, part i. p. 100).
- H. Behrens.—*Sur la Structure Microscopique et sur la Trempe de l'Acier et de la Fonte* (Recueil des travaux chim. des Pays-Bas, vol. x. p. 261, 1891).
- H. Wedding.—*Das Gefüge der Schienenköpfe* (Stahl und Eisen, vol. xi. p. 879, Nov. 1891).
- A. Martens.—*Die Mikrophotographische Ausrüstung der kön. mechanisch-technischen Versuchsanstalten* (Mittheil. aus den kön. technischen Versuchsanstalten, 1891, Heft 6, p. 278).
- P. H. Dudley.—*Microscopic Structure of Steel* (Journal of the New York Microscopical Society, Oct. 1891).
- A. Martens.—*Ueber Einige in der mechanisch-technischen Versuchsanstalt ausgeführte mikroskopische Eisenuntersuchungen* (Mittheil. aus den kön. technischen Versuchsanstalten, vol. x. p. 57, 1892, Heft 2).
- A. Martens.—*Die mikroskopische Untersuchung der Metalle* (Glaser's Annalen, vol. xxx. p. 201, 1892).
- H. Behrens.—*Revue Générale des Sciences Pures et Appliquées* (vol. iii. p. 343, May 15, 1892).
- A. Martens.—*Das Gefüge der Schienenköpfe* (Stahl und Eisen, vol. xii. p. 406, May 1, 1892).
- H. Wedding.—*Das Gefüge der Schienenköpfe* (Stahl und Eisen, vol. xii. p. 478, May 15, 1892).
- A. Martens.—*Das Gefüge der Schienenköpfe* (Stahl und Eisen, vol. xii. p. 530, June 1, 1892).
- G. Guillemin.—*Analyse Micrographique des Alliages* (Comptes Rendus de l'Académie des Sciences, vol. cxv. p. 232, July 25, 1892).
- Tetskichir Mukai.—*Studien über chemisch-analytische und mikroskopische Untersuchung des Manganstahls* (Freiberg, 1892).
- H. M. Howe.—*Note on Manganese-Steel* (Trans. Am. Inst. of Min. Eng., vol. xxi., 1892).
- F. Osmond.—*Sur la métallographie microscopique* (Rapport présenté à la Commission des méthodes d'essai des matériaux de construction, le 10 Février 1892; vol. ii., des travaux de la dite Commission, pp. 7-17, Paris, 1895).
- P. Kreuzpointner.—*The Microscopic Structure of Iron and Steel* (The Iron Age, 1892, p. 1224, June 23, 1892).
- G. Guillemin.—*Sur la métallographie microscopique des alliages du cuivre* (Rapport présenté à la Commission des méthodes d'essai des matériaux de construction le 5 Avril 1893; vol. ii., des travaux de la dite Commission, pp. 19-25).
- G. Charpy.—*Influence de la température de recuit sur les propriétés mécaniques et la structure du laiton* (Comptes Rendus, vol. cxvi. p. 1131, 15 Mai 1893).
- F. Osmond.—*Microscopic Metallography* (Transactions of the American Institute of Mining Engineers, vol. xxii. p. 243).
- A. Martens.—*The Micro-structure of Ingot Iron in Cast Ingots* (*ibid.*, vol. xxiii. p. 37).
- A. Sauveur.—*Micro-structure of Steel* (*ibid.*, vol. xxii. p. 546; Discussion of these last three papers, *ibid.*, vol. xxiii. p. 608).
- H. Wedding.—*Praktische Verwendung der Mikroskopie des Eisens* (Stahl und Eisen, vol. xiii. p. 974, Nov. 15, 1893).



- H. Behrens.—*Das mikroskopische Gefüge der Metalle und Legierungen* (Leopold Voss, Hamburg und Leipzig, 1894).
- H. Behrens.—*Sur l'acier cimenté, le ferro-chrome, le ferro-tungstène, l'acier chromé et l'acier tungstaté* (Recueil des travaux chim. des Pays-Bas, vol. xiii. p. 155, 1894).
- F. Osmond.—*Sur l'emploi du polissage dans l'étude de la structure des métaux* (Comptes Rendus, vol. cxviii. p. 807, 9 Avril 1894).
- J. O. Arnold.—*The Physical Influence of Elements on Iron* (Journal of the Iron and Steel Institute, 1894, part i. p. 107).
- J. E. Stead.—*Methods of preparing Polished Surfaces of Iron and Steel for Microscopic Examination* (Journal of the Iron and Steel Inst., 1894, part i. p. 292).
- J. O. Arnold and A. A. Read.—*The Chemical Relations of Carbon and Iron* (Journal of the Chemical Society, vol. lxxv. pp. 788-801, Aug. 1894).
- F. Osmond.—*Contribution à l'étude de la structure des aciers* (Comptes Rendus, vol. cxix. p. 329, 30 Juillet 1894).
- A. Martens.—*Die Mikroskopie der Metalle auf dem Ingenieur-Congress zu Chicago, 1893* (Stahl und Eisen, vol. xiv. p. 758, 1 Sept. 1894).
- H. Wedding.—*Neuer Apparat zur Aufnahme der Lichtbilder von Eisenschliffen* (Stahl und Eisen, vol. xiv. p. 857, 1 Oct. 1894).
- F. Osmond.—*Méthode générale pour l'analyse micrographique des aciers au carbone* (Bulletin de la Société d'Encouragement, 4<sup>e</sup> Série, vol. x. p. 480, Mai 1895).
- H. Wedding.—*Untersuchung eisenhüttenmännischer Erzeugnisse* (Stahl und Eisen, vol. xv. p. 506, 1 Juin 1895).
- A. Sauveur et A. Martens.—(Échange d'observations entre) sous le titre *Die Mikroskopie der Metalle auf dem Ingenieur-Congress zu Chicago, 1893* (Stahl und Eisen, vol. xv. p. 537, 1895).
- Capn. Houdaille.—*Sur une cause d'altération de l'aluminium* (Revue du génie militaire, Juillet 1895).
- Ch. Frémont.—*Sur un microscope spécial pour l'observation du corps opaques* (Comptes Rendus, vol. cxxi. p. 321, 12 Août 1895).
- A. Martens.—*Bericht der Unterkommission Nr. 15 der iv. ständigen Kommission für die Vereinbarung einheitlicher Prüfungsmethoden in Bau- und Konstruktionsmaterialien betreffs Würdigung des Prüfungsverfahrens des Kleingefüges der Metalle. Erörterung der Möglichkeit eines einheitlichen Prüfungsverfahrens* (Vorschläge, Zurich, 1895).
- F. Osmond.—*Sur la trempe des aciers extra-durs* (Comptes Rendus, vol. cxxi. p. 684, 11 Novembre 1895).
- J. O. Arnold.—*The Influence of Carbon on Iron* (Proceedings of the Institution of Civil Engineers, vol. cxxiii. p. 127, Dec. 3, 1895).
- J. E. Stead.—(Proceedings of the Cleveland Institution of Engineers, 1895, December, pp. 51-94?).
- Th. Andrews.—*Microscopic Internal Flaws in Steel Rails and Propeller Shafts* (Engineering, Jan. 17, 1896 (p. 91); Jan. 24, 1896 (p. 128); and Feb. 7, 1896 (p. 194), vol. lxi.).
- J. O. Arnold.—*Influence of Small Quantities of Impurities on Gold and Copper* (Engineering, Feb. 7, 1896, p. 176).
- G. Charpy.—*Recherches sur la alliages de cuivre et de zinc* (Bulletin de la Société d'Encouragement (5<sup>e</sup> Série), vol. i. p. 180, Février 1896).
- Arnold and Seaton.—*The Engineer*, March 27, 1896.
- H. Le Chatelier.—*Sur la métallographie microscopique* (Bulletin de la Société d'Encouragement (5<sup>e</sup> Série), vol. i. p. 559, Avril 1896).
- U. Le Verrier.—*Sur la micrographie des métaux* (Supplément à la Revue industrielle de l'Est du 31 Mai 1896).
- H. M. Howe and A. Sauveur.—*Further Notes on the Hardening of Steel* (Journal of the Iron and Steel Inst., 1896, part i. p. 170).
- A. Martens.—*Untersuchung über den Einfluss des Hitzegrades beim Auswalzen auf die Festigkeitseigenschaften und die mikroskopische Gefüge von Fluss-*



- eisenschienen* (Mittheilungen aus den kön. technischen Versuchsanstalten, xiv. Jahrgang, 1896, 2<sup>te</sup> Heft, p. 89).
- W. C. Roberts-Austen and F. Osmond.—*On the Structure of Metals, its Origin and Causes* (Philosophical Transactions of the Royal Society, vol. clxxxvii. pp. 417–432, and Bulletin de la Société d'Encouragement (5<sup>e</sup> Série), vol. i. p. 1136, Août 1896).
- A. Sauveur.—*The Micro-structure of Steel and the Current Theories of Hardening* (Am. Inst. Mining Engineers, Colorado Meeting, Sept. 1896).
- J. E. Stead.—*Micro-chemical Examination of Old Steel Rails and Tyres* (Iron and Steel Trades Journal, Dec. 19, 1896).
- G. Charpy.—*Appareils pour l'examen microscopique des corps opaques* (Revue générale des sciences pures et appliquées, vol. vii. p. 1260, 30 Décembre 1896).
- F. Osmond.—*La Métallographie considérée comme méthode d'essai* (Association internationale pour l'essai des matériaux, Congrès de Stockholm, 1897, and Metallographist, vol. i. p. 65).
- J. E. Stead.—*Microscopic Accessories* (Journal of the Iron and Steel Inst., 1897, i. p. 42).
- G. Charpy.—*Microscopic Study of Metallic Alloys* (Bulletin de la Société d'Encouragement, March 1897, and Metallographist, vol. i. p. 88).
- A. Sauveur.—*Constitution of Steel* (Technology Quarterly, June 1898; Metallographist, vol. i. p. 210).
- Howe and Sauveur.—*Relation of Temperature and Grain of Steel* (Engineering and Mining Journal, vol. lx. p. 537).
- J. E. Stead.—*Crystalline Structure of Iron and Steel* (Journal of the Iron and Steel Inst., 1898, i. p. 145).
- J. O. Arnold.—*Micro-chemistry of Cementation* (Journal of the Iron and Steel Inst., 1898, ii. p. 185).
- F. Osmond.—*Micro-structure of Nickel and Iron Alloys* (Comptes Rendus, May 9, 1898).
- J. E. Stead.—*Brittleness in Soft Steel by Annealing* (Journal of the Iron and Steel Inst., 1898, ii. p. 137).
- A. Sauveur.—*Relation between Structure and Thermal and Mechanical Treatment* (Journal of the Iron and Steel Inst., 1899, ii. p. 195).
- F. Osmond.—*New Reagents for Micro-work* (Metallographist, vol. iii. p. 1).
- H. Behrens.—*Antimonial Alloys for Axle Bearings* (Metallographist, vol. iii. p. 4).
- E. Heyn.—*Micro-structure of Steel* (Stahl und Eisen, August 1 and 15, 1899).
- E. Heyn.—*Micro-structure of Bronzes* (Translated in Journal of Franklin Inst., June 1899).
- E. H. Saniter.—*Allotropic Iron and Carbon* (Journal of the Iron and Steel Inst., 1898, i. p. 206).
- Ewing and Rosenhain.—*Crystalline Structure of Metals* (Phil. Trans. Roy. Soc., vol. cxcliii. p. 353, and vol. cxcv. p. 279).
- F. Osmond.—*Crystallography of Iron* (Annales des Mines, Jan. 1900).
- J. E. Stead.—*Practical Metallography* (Proceedings of Cleveland Institute of Engineers, February 26, 1900, and Metallographist, vol. iii. p. 220).
- G. Charpy.—*Micro-structure of Metals* (Bulletin de la Société d'Encouragement, June 1898).
- Le Chatelier.—*Technology of Metallography* (Metallographist, vol. iv. p. 1).
- A. Stansfield.—*The Present Position of the Solution Theory of Carburised Iron* (Journal of the Iron and Steel Inst., 1899, ii. p. 169; also 1900, ii. p. 317).
- H. Le Chatelier.—*Application of the Law of Phases to Alloys and to Rocks* (Comptes Rendus, Jan. 8, 1900).
- B. Roeseboom.—*Iron and Steel from the Point of View of the "Phase Doctrine"* (Journal of the Iron and Steel Inst., 1900, part ii. p. 311).

- F. Osmond.—*Iron and Steel from the Point of View of the "Phase Doctrine"* (Bull. de la Soc. d'Encourag., Nov. 30, 1900).
- H. Le Chatelier.—*Iron and Steel from the Point of View of the "Phase Doctrine"* (Bull. de la Soc. d'Encourag., Nov. 30, 1900).
- W. Campbell.—*Crystallisation produced in Solid Metal by Pressure* (Metallographist, vol. iv. p. 57).
- C. H. Heycock and F. H. Neville.—*On the Results of Chilling Copper-Tin Alloys* (Proc. Roy. Soc., vol. lxxviii.).
- J. E. Stead.—*Metallic Alloys* (Cleveland Institution of Engineers, Dec. 10, 1900).
- Hannover.—*Casting on Mica* (Bulletin de la Société d'Encouragement, August 1901).
- Hannover.—*Contribution à l'étude des Alliages* (Société d'Encouragement, 1901).
- Baron Hans Jüptner von Jonstorff.—*Iron and Steel from the Point of View of the "Phase-Doctrine"* (Journal of the Iron and Steel Inst., 1901, vol. i. p. 229).
- E. Heyn.—*Short Reports from the Metallographical Lab. of the Royal Testing Inst. of Charlottenburg* (International Assoc. for Testing Materials, Budapest Congress, 1901).
- A. Sauveur.—*Structure and Finishing Temperature of Steel Rails* (Amer. Section of the International Assoc. for Testing Materials, June 1902; Metallographist, vol. v. p. 197).
- G. Charpy and L. Grenet.—*The Equilibrium of Iron-Carbon Systems* (Bull. de la Soc. d'Encour., March 1902).
- W. Campbell.—*The Structure of Metals and Binary Alloys* (Journal of the Franklin Inst., July, Aug., and Sept. 1902).
- J. A. Ewing and J. C. W. Humfrey.—*Fracture of Metals under Repeated Alternations of Stress* (Phil. Trans., Nov. 20, 1902).
- W. C. Roberts-Austen and T. K. Rose.—*Alloys of the Gold-Silver Series* (Proc. Roy. Soc., vol. lxxi., 1903, p. 161).
- H. M. Howe.—*Constitution of Cast Iron* (Amer. Soc. for Testing Materials, June 1902).
- A. H. Sirks.—*Etching of Metals by means of Electric Current* (Konink. Akad. Wetensch. Amsterdam, Jan. 28, 1902, p. 217).
- M. A. Richards.—*Technical Photo-microscopy of Metals* (Journ. of Applied Microscopy, Aug. 1902).
- J. C. W. Humfrey.—*Effect of Strain on the Crystalline Structure of Lead* (Phil. Trans. vol. cc. pp. 225-240).
- G. Beilby.—*Surface Structure of Solids* (Journ. Soc. Chem. Ind., xxii. pp. 1166-1177, Nov. 16, 1903).
- T. C. Heycock and F. H. Neville.—*Constitution of Copper-Tin Alloys* (Phil. Trans., ccii. pp. 1-69, Oct. 2, 1903).
- G. Beilby.—*Hard and Soft States in Metals* (Phil. Mag., viii. pp. 258-276, Aug. 1904).
- J. A. Ewing.—*Structure of Metals* (Nature, lxx. p. 187; Abstract of Rede Lecture before the University of Cambridge, June 11, 1904).
- E. S. Shepherd.—*Constitution of Copper-Zinc Alloys* (Journ. Phys. Chem., viii. pp. 421-435, June 1904).
- W. Rosenhain.—*Observations on Slip-bands* (Roy. Soc. Proc., lxxiv. pp. 557-562, Apr. 10, 1905).
- L. Guillet.—*Classification of Steel Alloys* (Rev. de Métallurgie, May 1905, pp. 350-367).
- H. le Chatelier.—*Technique of Metallography* (Rev. de Métallurgie, pp. 528-537, July 1905).
- O. F. Hudson.—*Micro-structure of Brass* (Journ. Soc. Chem. Ind., vol. xxv. p. 503).
- H. C. H. Carpenter, R. A. Hadfield, and P. Longmuir.—*Iron-Nickel-Manganese-Carbon Alloys* (Seventh Report of the Alloys Research Committee, Inst. Eng. Mech. Proc., iv. pp. 857-959).

- F. Osmond and G. Cartaud.—*Crystallography of Iron* (Metallurgie, iii. pp. 522-545, Aug. 8, 1906; Journal of the Iron and Steel Inst., 1906 vol. iii. pp. 444-449).
- J. A. Ewing.—*Molecular Structure of Metals* (Phil. Mag., xii. pp. 256-267, Sept. 1906).
- E. Heyn.—*Etching of Iron and Mild Steel for Investigation of Macro-structure* (Paper read before International Assoc. for Materials, Brussels, 1906).
- A. Sauveur.—*Constitution of Iron-Carbon Alloys* (Journal of the Iron and Steel Inst., 1906, vol. iv. pp. 493-519).
- E. S. Shepherd and E. Blough.—*Constitution of Copper-Tin Alloys* (Journ. Phys. Chem., x. pp. 630-658, Nov. 1906).
- L. Guillet.—*Relation between Constitution and Ductility of Alloys* (Comptes Rendus, cxliv. pp. 1273-1275, June 10, 1907).
- W. Rosenhain.—*Deformation and Fracture of Iron and Mild Steel* (Journal of the Iron and Steel Inst., 1906, No. 2, p. 189).
- F. W. Hinrichsen and O. Bauer.—*Micro-chemical Detection of Sulphur, Selenium, and Tellurium in Copper* (Metallurgie, iv. p. 315, May 22, 1907; see also Metallurgie, iii. p. 73, Feb. 1906).
- F. Rogers.—*Microscopic Study of Strain in Metals* (Roy. Microscopic Soc. Journ., pp. 14-18, 1907).
- J. A. Ewing.—*Structure of Metals* (Manchester Lit. and Phil. Soc., Mem. 51, 15, pp. 1-20, July 30, 1907).
- E. A. Lewis.—*Heat Treatment of Brass and Bronze* (Journ. Soc. Chem. Ind., xxvii. pp. 479-481, May 30, 1908).
- W. Rosenhain.—*Study of Breakages* (Engineering, lxxxvi. pp. 340-344, Sept. 11, 1908).
- F. W. Harbord.—*Action of Toothless Circular Saws* (Engineer, cv. p. 187, Feb. 21, 1908).
- P. Goerens.—*Use of Colour Photography in Metallography* (Metallurgie, v. pp. 19-23, Jan. 8, 1908).
- G. D. Bengough and O. F. Hudson.—*Heat Treatment of Copper-Zinc Alloys* (Journ. Soc. Chem. Ind., xxvii. pp. 43-52, Jan. 31, 1908).
- E. F. Law.—*Non-metallic Impurities in Steel* (Journal of the Iron and Steel Inst., 1907, No. 2, pp. 94-105).
- W. Campbell.—*Effect of Work and Heat Treatment on the Structure of Metals* (Metallurgie, 1907, iv. pp. 801-809, Dec. 8, and pp. 825-834, Dec. 22).
- G. M. Gulliver.—*Text-book on Metallic Alloys* (C. Griffin & Co., Ltd.).
- P. Goerens.—*Introduction to Metallography*. Translated by F. Ibbotson (Longmans & Co.).
- E. F. Law.—*Text-book on Alloys and their Industrial Application* (C. Griffin & Co., Ltd.).

## CHAPTER VII.

### FUEL.

**Classification of Fuel.**—The term fuel is applied to substances that may be burned by means of atmospheric air with sufficient rapidity to evolve heat capable of being applied to economic purposes. In some cases the products of combustion are used for effecting metallurgical reactions, while in others the fuel is consumed simply for the sake of the heat generated.

Fuels may be of ancient or modern origin, and may be divided into two classes—(I.) Natural fuels, and (II.) Prepared fuels.

The first class includes—(1) wood and the various kinds of mineral fuel, (2) turf or peat, (3) lignite, (4) bituminous coal, and (5) anthracite. Besides these, various liquid hydrocarbons, such as petroleum, are found in sufficient quantity to render their employment possible on a large scale. At Pittsburg in Pennsylvania and at other localities combustible gas occurs naturally, and in the United States is largely used for metallurgical purposes.

The second class includes—(1) compressed fuels, which are composed of more or less pulverulent material consolidated into bricks, with or without cementing agents; (2) dried fuels, or those in which the water and a certain proportion of the more volatile constituents have been expelled by heat, examples being afforded by wood, lignite, and peat; (3) carbonised fuels, such as coke and charcoal; (4) liquid fuels, obtained by distillation or as by-products; and (5) gaseous fuels, obtained (*a*) by the distillation, partial or entire, of natural fuels, or (*b*) by their incomplete combustion.

The value of all these fuels depends upon the amount of carbon and hydrogen they contain. The majority of them contain oxygen, nitrogen, sulphur, and phosphorus, as well as a certain amount of inorganic material which ultimately forms the ash. The amount and nature of this ash is of great importance, and it will be evident that if the fuel can be deprived of its ash-giving constituents by treatment before combustion its value will be



greatly increased. The hydrogen that is in excess of the quantity required to form water with the oxygen in the fuel is alone available for combustion, and is termed the available hydrogen. The remainder of the hydrogen is regarded as being already in combination as water, and may be viewed as an actual source of loss, because this water has to be vaporised when the fuel is burned. Cellulose ( $C_6H_{10}O_5$ ) contains no available hydrogen, whilst cannel coal contains a considerable quantity.

The temperature at which fuels kindle varies considerably. Slow oxidation may, it is true, take place at ordinary temperatures, but in metallurgical practice it is only comparatively rapid combustion that is really useful. Extreme density and, on the other hand, great tenuity equally hinder inflammability. For the former reason, anthracite, diamond, and graphite are ignited with great difficulty. Fuels richest in hydrogen are the easiest to ignite, the inflammability of resinous wood and of bituminous coal being due to this fact. Combustible gases, however, do not ignite below a cherry-red heat, on account of the extreme dispersion of their molecules.<sup>1</sup> The inflammability of vegetable charcoal depends upon the temperature at which it is prepared. Thus, when wood is carbonised at  $300^\circ$  to  $400^\circ$ , the charcoal ignites at  $360^\circ$ ; and when a temperature of  $1200^\circ$  to  $1300^\circ$  has been employed, ignition cannot be effected below  $600^\circ$  to  $800^\circ$ . This is due to the fact that the hydrogen is driven off almost entirely at the higher temperatures. Peat ignites at  $225^\circ$ ; pine wood at  $295^\circ$ ; ordinary coal at  $325^\circ$ ; coke, anthracite, hydrogen, and carbonic oxide at a dull-red heat.

The length of flame given by fuel in burning is so important that coals have advantageously been classed as "long-flaming" and "short-flaming." Certain fuels disengage at the moment of combustion a large proportion of volatile matter, and these constitute the long-flaming varieties. The manner in which the fuel is burned, however, has a great effect upon the flame. Charcoal, for example, if burned with free access of air, merely glows; but if burnt with a limited supply of air in a thick layer so arranged that the products of combustion from the lower portion pass through the upper, carbonic oxide will be formed, which will burn with a blue flame. The volume of the flame depends, amongst other conditions, upon the velocity of the current of air by which the combustion is effected, the volume decreasing as the velocity rises.

**Calorific Power.**—The calorific power of a fuel is the total heat generated by the combustion of a unit of weight of the fuel. The heat is measured in two ways, either by the number of units of weight of water raised  $1^\circ$ , or by the number of units of water evaporated. The latter method, which was proposed by Prof.

<sup>1</sup> Frankland, *Phil. Mag.*, vol. xxxvi. (1868), p. 309. See also Ernst, *Chemisches Repertorium*, vol. xvii. p. 2.

Rankine, gives numerical results equal to the former divided by 537 when the centigrade scale is used. In expressing the calorific power of a fuel, the amount of heat generated on the combustion of carbon to carbonic anhydride is taken as the standard of comparison. This calorific power of carbon is expressed by the number of parts by weight of water capable of being heated from  $0^{\circ}$  to  $1^{\circ}$  C. by the combustion of one part by weight of carbon. It is found by direct experiment to be 8080 units. The unit of heat varies with the thermometric scale and the unit of weight employed. The unit most largely adopted, the metric unit or *large calorie*, is the quantity of heat required to raise 1 kilogram of water from  $0^{\circ}$  to  $1^{\circ}$  C.; whilst the British thermal unit is the amount of heat required to raise 1 lb. of water  $1^{\circ}$  Fahr. Thus 1 *calorie* = 3.96832 British units, and 1 British unit = 0.251996 *calorie*. Expressed in equivalent foot-pounds, 1 *calorie* = 1390.

For experimentally determining the calorific power of a fuel, a **calorimeter** is employed. Count Rumford's calorimeter consisted simply of a vessel filled with water, containing a worm-pipe through which the products of combustion passed from a funnel outside. In this way they imparted their heat to the water, whose rise in temperature was noted. All calorimeters are similar in principle to Rumford's. In the more modern instruments, however, the vessel in which the combustion takes place is entirely surrounded by water and by an air jacket.<sup>1</sup>

If a fuel consists only of carbon and hydrogen, its calorific power may be calculated by multiplying the weight of each of the elements in one part of the fuel by their respective calorific powers as found by experiment. For example, a fuel consists of 85.71 per cent. of carbon and 14.29 per cent. of hydrogen. What is its calorific power? The calorific powers of carbon and hydrogen are respectively 8080 and 34,462, and

$$\begin{aligned} 85.71 \times 8080 &= 692536.80 \\ 14.29 \times 34462 &= 492461.98 \end{aligned}$$

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$$1184998.78$$

which is the heat evolved on the combustion of 100 parts of the fuel. This, when divided by 100, gives 11849.98 as the calorific power of the fuel. So simple a case as this is rarely met with, it being usually necessary to determine the amount of available hydrogen in the fuel, and to multiply the result by 34,462.

When a compound is burned in oxygen or air, the heat evolved is not the same as would be evolved by the combustion of proportional weights of the constituent elements in the free condition, but may be either greater or less, according to whether the body

<sup>1</sup> On calorimeters, consult *Gas and Fuel Analysis*, A. Gill, 1901; *The Calorific Power of Fuels*, H. Poole, 1905; *Fuel, Water, and Gas Analysis*, J. B. C. Kershaw, 1907.

was formed with absorption or evolution of heat, and the difference will be the heat of formation of the body. In the case of solid fuels, the heat of formation of the different constituents is quite unknown, and it is usual, in calculating the calorific power, to assume that the constituents give out in burning the same amount of heat they would do if in the free state.

For commercial purposes, actual experiment is the best method for obtaining the calorific power of fuels.

**Calorific Intensity.**—The calorific intensity or pyrometric effect of a fuel is the highest temperature which the fuel is capable of producing when burnt in air. Measurements of calorific intensity are based on the fact that the heat produced by combustion is transferred to the product of combustion, and it may be determined by calculation on the assumption that the calorific intensity of a simple combustible body burnt in oxygen is equal to its calorific power divided by the product of the relative weight of its products of combustion and the specific heat of those products, or, expressed as an equation,

$$t^{\circ} = \frac{W \times C}{w \times c},$$

where  $W$  represents the weight of the substance,  $C$  the calorific power of the substance,  $w$  the weight of the product of combustion, and  $c$  its specific heat. For example, the calorific intensity of carbon burnt to carbonic anhydride in oxygen is—

$$\frac{12 \times 8080}{(12 + 32) \times 0.22} = 10016^{\circ}.$$

The calorific intensity of carbonic oxide burnt to carbonic anhydride is—

$$\frac{28 \times 2403}{(28 + 16) \times 0.22} = 6950^{\circ}.$$

If the substance is a mixture, the weights and specific heats of the various products of combustion must be introduced. In determining the calorific power of hydrogen, the water obtained is assumed to be in the liquid state. In determinations of the calorific intensity, however, the water is in the form of gas. From the calorific power, therefore, must be subtracted the amount of heat which would be given out on cooling the steam to  $0^{\circ}$ . For one part of water at  $100^{\circ}$  this would be 537 calories. Again, in raising the product of combustion from  $0^{\circ}$  to  $t^{\circ}$ , a greater amount of heat will be needed to raise it the first  $100^{\circ}$  while that product is liquid than would have been required if it had been gaseous. These two amounts of heat are in the proportion of the specific heats of steam and water, that is, as 0.4805 is to 1. Hence the extra quantity of heat to be added



to the 537 *calories* is  $(1 - 0.4805) 100$ , or 51.95 *calories*. The calorific power must therefore be decreased by  $(51.95 + 537) 9$ , or 5300.5 *calories*, since 1 part of hydrogen yields 9 parts of water. Hence the calorific intensity of hydrogen is—

$$\frac{1 \times (34462 - 5300.5)}{9 \times 0.4805} = 6743^\circ.$$

The calorific intensity is merely a theoretical quantity, as it is based on the assumptions that the products of combustion of the fuel have constant specific heats for all temperatures, and that they absorb all the heat produced. Neither of these assumptions is true, inasmuch as the specific heats of gases generally increase with the temperature and there is a considerable amount of heat lost by conduction and by radiation; dissociation also limits the temperature. The computation of calorific intensity has consequently but little commercial value.

The calorific intensity of a fuel may be found by direct experiment by means of *pyrometers*.

## I. NATURAL FUELS.

1. **Wood.**—When dry, wood consists of 96 per cent. of woody tissue (cellulose,  $C_6H_{10}O_5$ ) and 4 per cent. of sap. A small proportion of inorganic matter is also present, and, when recently felled, all wood contains a large proportion of water. The mean composition of well-dried wood is—

Carbon.	Hydrogen.	Oxygen.	Nitrogen.
50.0	6.0	42.0	2.0

—or, roughly, 50 per cent. of carbon and 50 per cent. of chemically combined water. Air-dried wood contains 40 per cent. of carbon, 40 per cent. of chemically combined water, and 20 per cent. of hygroscopic water. The proportion of ash-giving constituents varies from 1.2 to 2.3 per cent., the average percentage being 1.5. The ash consists of about 70 per cent. of calcium carbonate, 20 per cent. of alkaline carbonates, together with varying amounts of alkaline sulphates and chlorides, silica, phosphoric anhydride, magnesia, ferric oxide, manganous oxide, and alumina. The specific gravity of wood varies considerably. Air-dried woods, with 20 per cent. of moisture, having a specific gravity of more than 0.55, are classed as *hard*; with a lower specific gravity they are classed as *soft*. After the air has been completely expelled from the pores of the wood, the specific gravity is in all cases nearly the same, varying only from 1.48 to 1.53. The calorific intensity of wood is small, but its combustibility and the amount of flame it gives are very great. The large percentage of hygroscopic water renders wood unsuitable as a fuel in cases where



high temperatures are required, and the rapid demolition of forests tends to increase its cost.

2. **Peat.**—Peat or turf is the product of the slow decay of plants under conditions in which the supply of air is limited. It is formed chiefly from the mosses *Sphagnum* and *Hypnum*, with other plants. It may be classed, according to the localities where it has been produced, as highland and lowland peat, according to its age as recent peat, and as old peat with only traces of organic texture, and, lastly, according to the mode in which it has been extracted, as "cut peat" or "dredge peat."

Peat deposits are widely distributed throughout the world. In Ireland it is estimated that the peat area is not less than one-seventh of the island. That of Great Britain covers six million acres, with an average depth of 12 feet. Extensive deposits are met with in the United States, Canada, and Russia, where peat is of metallurgical importance, in North Germany, Austria, and Scandinavia.

The composition of peat is extremely variable, the proportion of water and of ash-giving constituents having so great an influence that it is almost impossible to estimate its average composition. The best air-dried peat still contains 25 per cent. of hygroscopic water. From numerous analyses, the composition of pure peat, exclusive of moisture, has been found to be as follows:—

Carbon.	Hydrogen.	Oxygen.	Nitrogen.
49·6 to 63·9	4·7 to 6·8	28·6 to 44·1	0·0 to 2·6

—in which the ratio of the oxygen (with the nitrogen) to the hydrogen is as 5 or 6 : 1.

The proportion of ash-giving constituents varies from 1 to 30 per cent. and more, being rarely below 10 per cent. The ash consists chiefly of lime, ferric oxide, and silica, together with phosphoric acid, sulphuric acid, and carbonic acid, and, in considerable quantities, alkalies, alumina, and magnesia. Raw peat also frequently contains iron pyrites. The high percentage of ash and of water, together with its bulk, are the main objections to the use of peat as fuel. For an equal evaporative power, its bulk is from 8 to 18 times that of coal.

Numerous methods have been adopted for freeing peat from ash and moisture. They consist chiefly in the subdivision of the peat into minute fragments. These are washed and dried, with or without compression.

The calorific power of peat varies inversely as the amount of water and ash it contains. For peat without ash and water, the calorific power is 5237, whilst for ordinary air-dried peat it does not exceed 3000.

The specific gravity of peat varies, with the proportion of ash and the mode of preparation, from 0·25 to 1·4.

3. **Lignite.**—Brown-coal and lignite occupy an intermediate place between peat and true coals, there being no abrupt break in the compositions. Indeed, the transition from woody tissue to anthracite is gradual, as is well shown by the following tabular statement, in which the carbon is represented as a constant quantity :—

	Carbon.	Hydrogen.	Oxygen.
Wood . . . . .	100	12·18	83·07
Peat . . . . .	100	9·85	55·67
Lignite . . . . .	100	8·37	42·42
Bituminous coal . . . . .	100	6·12	21·23
Anthracite . . . . .	100	2·84	1·74

(Percy.)

The term “lignite” is used by British and American writers as synonymous with the brown-coal of the Germans. It is usually applied to those varieties of coal which are older than peat and more recent than the coals of carboniferous age. Many writers, however, erroneously confine the term “lignite” or “brown-coal” to coals of the Tertiary epoch. Four fairly distinct types of lignite may be distinguished :—(1) Fossil wood, fibrous brown-coal, the lignite of the Germans, which has a distinct ligneous texture ; (2) Earthy lignite, without structure and earthy in fracture ; (3) Conchoidal lignite, without any distinct vegetable structure, and with a conchoidal fracture ; (4) Bituminous lignite, a black, shiny fuel, sometimes resembling anthracite, and having a conchoidal or earthy fracture. For metallurgical purposes the first three types only are of importance, the fourth type being used more frequently as material for the production of tar than as a fuel.

When recently raised from the mine, lignites contain as much as 33 per cent. of moisture, and even more. When air-dried, however, they lose half this amount. The proportion of ash varies from 3 to 30 per cent. The ash contains lime, alumina, and silica, together with magnesia, some alkalis, and ferric oxide, and an appreciable quantity of sulphuric acid, but, as a rule, no phosphoric acid. The mean percentage composition of lignite is as follows :—

Variety.	Carbon.	Hydrogen.	Oxygen.
1. Fibrous . . . . .	57 to 67	5 to 6	28 to 37
2. Earthy . . . . .	45 to 70	5 to 6	25 to 30
3. Conchoidal . . . . .	65 to 75	4 to 6	21 to 29
4. Bituminous . . . . .	70 to 80	6 to 8	12 to 24

Lignite burns with a long, smoky flame. The calorific power varies considerably, the mean calorific power of the four varieties being — (1) 5000, (2) 5700, (3) 6500, and (4) 7000 *calories* respectively. The value of lignite as fuel would thus appear to be considerable, but in practice complete desiccation is hardly attainable, and a high percentage of moisture is always retained. The only practical method of increasing the calorific power of lignite is by removing this moisture, and for this purpose drying in air, heating in kilns, or compression has been attempted with considerable success.<sup>1</sup>

Lignite, however, is very little used for metallurgical purposes, except in districts where no other fuel is available.

4. **Coal.**—Coals formed previously to the Cretaceous period are distinguished from lignites by their deep-black streak, great density, and friability. The fracture is more lamellar, the ligneous texture having disappeared. When subjected to dry distillation they yield a greater amount of carbonaceous residue, and the condensed products contain less water than is the case with fuels of more recent age. Coals contain very little water, and when dried at 100° they are considerably less hygroscopic than wood and lignite. The specific gravity of pure coal, with a low percentage of ash, varies from 1·2 to 1·4, the density being in direct proportion to the percentage of carbon. A cubic yard of coal averages 18 cwt. in weight. The proportion of coke left on distillation varies from 50 to 90 per cent., and the composition of coal varies within the following limits :—

Carbon.	Hydrogen.	Oxygen.
75 to 93	6 to 4	19 to 3

With the oxygen is included 1 to 2 per cent. of nitrogen. In coals, the ratio of the oxygen (with the nitrogen) to the hydrogen varies between the wide limits of 1 : 1 to 4 : 1.

Coals may be classified according to the length of the flame and the character of the residue which is left when they are subjected to dry distillation. The old classification, based solely on the character of the coke produced, divided coals into two classes, *caking* and *non-caking*, according as the coke produced formed a compact or pulverulent mass. Percy classed coal into three varieties—(1) non-caking or free-burning, rich in oxygen; (2) caking; (3) non-caking, rich in carbon. This classification is based on the chemical composition of the coals, and therefore on their calorific power. Grüner was led to adopt a more detailed classification, in which five types are distinguished :—

(1) *Non-caking Coals with Long Flames.*—These coals, which most closely approach lignites, when subjected to dry distillation yield 55 to 60 per cent. of pulverulent coke, the evolution of

<sup>1</sup> Zincken, *Physiographie der Braunkohle*, Hanover, 1867-71.

volatile gases giving rise to a long, smoky flame. The composition varies within the following limits:—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
75 to 80	4.5 to 5.5	15.0 to 19.5

—the ratio of the oxygen to the hydrogen being 3:1 or 4:1. The calorific power generally varies from 8000 to 8500. Coals of this type are of common occurrence in Scotland, Derbyshire, and Staffordshire.

(2) *Caking, Long-flame Gas-coal.*—Coals of this type contain—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
80 to 85	5 to 5.8	10 to 14.2

—the ratio of the oxygen to the hydrogen being 2:1 or 3:1. They yield on slow distillation 60 to 68 per cent. of caked, but very friable and porous, coke, and 32 to 40 per cent. of volatile matter, of which 17 to 20 per cent. is gas. The calorific power generally varies from 8500 to 8800.

(3) *Bituminous or Furnace Coal.*—These coals are black, not very hard; they burn with a smoky flame, at the same time softening and intumescent in the fire. They contain—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
84 to 89	5 to 5.5	5.5 to 11

—the ratio of the oxygen to the hydrogen being 1:1 or 2:1. They yield 68 to 74 per cent. of caked and swollen coke, and 15 to 16 per cent. of gas. The calorific power varies from 8800 to 9300.

(4) *Caking Coals with Short Flame.*—These contain—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
88 to 91	4.5 to 5.5	5.5 to 6.5

—the ratio of the oxygen to the hydrogen being 1:1. They yield 74 to 82 per cent. of caked and very compact coke, and 12 to 15 per cent. of gas. The calorific power varies from 9300 to 9600.

(5) *Anthracitic Coals.*—These burn with a short flame, and have the following composition:—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
90 to 93	4 to 4.5	3 to 5.5

—the ratio of the oxygen to the hydrogen being 0.5:1 or 1:1. These coals form the transition to true anthracites. On coking, they yield 82 to 92 per cent. of pulverulent or fritted coke, and 12 to 8 per cent. of gases. The calorific power varies from 9200 to 9500. Coals of this type are met with in South Wales and in Pennsylvania.

The percentage of ash yielded by the several varieties of coal ranges from 1 to 30, but seldom exceeds 7. The ash consists



mainly of silica, with alumina, lime, magnesia, ferric oxide, and manganic oxide. Sulphur is also frequently present, but the proportion of phosphorus is usually inconsiderable.

5. **Anthracite.**—This is the ultimate product of the conversion of vegetable matter into coal. Its colour is jet black, with a vitreous lustre; its structure homogeneous, and its fracture conchoidal.

The mean of a large number of analyses gave the following as the composition of true anthracite, free from ash:—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
93 to 95	2 to 4	3·0

The proportion of nitrogen varies from 0·55 to 2·85 per cent.; and the ratio of the oxygen to the hydrogen 1 : 1 to 1 : 0·5. Anthracite burns almost without flame, and the carbonaceous residue remaining after distillation shows no signs of caking. The anthracite of Pennsylvania is employed on a large scale in the manufacture of pig-iron. In the United Kingdom this is not the case, as our anthracites will not stand a high temperature without disintegration.

It must be borne in mind that “coal” is a popular rather than a scientific name, as it is frequently applied not only to beds of fossilised vegetation, but to all mineral substances capable of being used as fuel. According to Frémy,<sup>1</sup> true coal may be distinguished from lignites by its insolubility in hypochlorites, and its very imperfect solubility in nitric acid.

Coals having widely different properties may be proved by analysis to contain exactly the same amounts of carbon, hydrogen, and oxygen, so that in the respective cases the grouping of these elements must vary greatly. Coals, in fact, may be isomeric.

It is found that the calorific power of true coal and lignites increases with the proportion of coke left by distillation, and the student will do well to bear in mind that the calorific value of a coal may be better estimated by weighing the coke left after strongly heating the coal in a covered crucible, and taking into consideration the percentage of ash, than by calculations based on a chemical analysis of the sample. The class to which the coal belongs may also be best determined by this method of distillation in a closed vessel, which enables the relative amounts of water, bituminous matter, and coke to be ascertained. The method of coking in a covered crucible also gives valuable information as to the nature of the coke.

6. **Liquid Fuels.**—Under the general term of *petroleum* is included a series of natural hydrocarbons. These usually occur in nature impregnating clay, marl, sand, and schist, sometimes sufficiently to render the rock combustible. The high percentage of ash in such fuels prevents them from being used direct, and, as a

<sup>1</sup> *Comptes Rendus*, vol. lii. (1861), p. 114.

rule, renders it necessary to subject them to distillation, which yields tar products, oils, and gases. The so-called "Boghead mineral," a bituminous schist of the Scotch coal measures, yields—

Ash.	Fixed Carbon.	Combustible Gases.
19·60	10·13	70·10

*Cannel coal* is a fuel of a similar character, but with a low percentage of ash. It burns with a long, smoky flame, and has the following percentage composition:—

Carbon.	Oxygen.	Hydrogen.	Ash.
85·0	8·0	5·0	2·0

It yields 42 per cent. of volatile matter. When the bituminous constituents of these rocks occur in sufficient quantity, naphtha and petroleum springs, or deposits of solid asphalt, are formed. At Baku in the Caspian Sea and in Pennsylvania mineral oils are obtained in enormous quantities by means of deep boreholes. The oil regions of the United States produced in 1906 over 130,000,000 barrels, each of 42 gallons, and in the same year Russia produced over 7,000,000 metric tons, equal to 50,000,000 42-gallon barrels.

Petroleum contains a very high proportion of hydrogen. On distillation from crude petroleum a product is obtained containing 79·82 to 88·5 per cent. of carbon and 11·5 to 20·18 per cent. of hydrogen. The boiling-point of petroleum varies from 110° to 280°, and the calorific power of the crude oil is 10,000 *calories*, a calorific power which is greater than that of refined oil.

The oil is employed in practice by burning it in a trough, by effecting its combustion in a spray or finely divided form by injecting it with a jet of steam or air, or by converting it into gas before combustion.<sup>1</sup>

**7. Natural Gas.**—In the oil regions of Pennsylvania and of the adjoining States, natural gas issues from the strata at a depth of 500 to 2000 feet below the surface; and when boreholes are sunk to the accumulated gas, it rises under a pressure of some 200 lbs. per square inch. When first reached, the gas is sometimes evolved at the enormous pressure of 1000 lbs. per square inch. Compared with air, the gas has a density of 0·45 to 0·55, and varies in volumetric composition within the following limits:—

CH <sub>4</sub> .	H.	N.	C <sub>2</sub> H <sub>6</sub> .	C <sub>2</sub> H <sub>4</sub> .	CO <sub>2</sub> .	CO.
60 to 80	5 to 20	1 to 12	1 to 8	0 to 2	0·3 to 2	trace

It has a calorific power of 14,000 to 15,600 *calories*, and a calorific intensity of 2745° to 2765°. Natural gas has long been used in

<sup>1</sup> On petroleum, consult Redwood, *Petroleum and its Products*, C. Griffin & Co., Ltd., 1907.

Pennsylvania to a limited extent for heating purposes. Since 1883, however, it has attained a remarkably rapid development for industrial purposes, and is now largely used in Pittsburg for metallurgical purposes.

The territory containing the source of natural gas includes a section of country extending from Western New York, through Pennsylvania, into West Virginia and Ohio, and to Canada.

## II. PREPARED FUELS.

1. **Compressed Fuels.**—Numerous attempts have been made to prepare a good fuel by mixing some binding material with small coal in proportions sufficient to enable the particles to cohere so as to be pressed into a block or *briquette*. Potato-meal, soluble glass, asphalt, and turpentine have been used as binding materials, but abandoned, whilst coal-tar and pitch have been successfully used for the purpose.

2. **Dried Fuels.**—The advantages derived from the expulsion of the water and a certain proportion of the more volatile constituents of wood, peat, and lignite have already been pointed out.

3. **Carbonised Fuels.**—On heating fuels without access of air, their constituents rearrange themselves in the form of solid, liquid, and gaseous compounds. For metallurgical purposes, the object of this operation is often only to obtain the solid constituent, charcoal or coke, which consists of carbon with subordinate amounts of hydrogen, oxygen, and ash-giving constituents, and which has a high calorific intensity. At the same time, the by-products obtained during the carbonisation are frequently utilised. The carbonised fuels to be considered are—(a) charcoal, and (b) coke.

(a) **Charcoal.**—This name is given to the carbonised residue remaining after the dry distillation of wood. When wood is heated to 200° without access of air it remains unaltered; at 220° it becomes brown; and at 270° to 300° it suffers decomposition, torrefied wood (*Rothholz*) being formed. At 350° it is resolved into a fixed residue, or charcoal, and volatile products. Good charcoal prepared at a temperature of 350° to 400° retains the structure of the wood from which it was derived, the volume being less. It is black, porous, and burns without smoke, and, in separate pieces, without flame. The specific gravity of porous charcoal varies from 0.28 to 0.54 according to the nature of the original wood and the temperature at which it was made. Charcoal prepared at 350° is considerably lighter than that prepared at the melting-point of platinum. Hard woods give a dense and heavy charcoal, whilst soft woods give soft and friable charcoal. The chemical composition also varies considerably, the percentage composition of charcoal



prepared at 340° (I.), and at the melting-point of platinum (II.), being as follows:—

Carbon.	Hydrogen.	Oxygen and Nitrogen.
I. 75·20	4·41	19·96
II. 96·52	0·62	0·94

The ash of the first charcoal was 0·48, and of the second 1·94 per cent. On an average, dry charcoal contains 90 per cent. of carbon, 3 per cent. of hydrogen, and 7 per cent. of oxygen and nitrogen.

The charcoal used in metallurgical operations is prepared by various methods, which may be divided into two groups—viz. methods of charring (1) in the open air and (2) in closed chambers. For charcoal-burning in the open air a suitable site is necessary. This should be dry, and sheltered from any prevailing wind. Water should be at hand for quenching the charcoal when made. The wood employed must be mature, cut while free from sap, barked, and air-dried for some months.<sup>1</sup>

When the charring is effected in circular piles, or *meilers*, the bed is made to slope from the circumference to the centre at an inclination of 1 in 15. Three stakes, 10 to 15 feet high, are driven in near the centre, so as to form a central triangular chimney. Around this, the timber, cut into suitable lengths, is stacked horizontally and radially. The mass is then covered with a mixture of fine charcoal and clay, and then with sods, with the grassy side inwards. To keep this covering up, wedges are driven in, and props put in so as to form hoops around the lower part of the pile. Brushwood is then thrown down the chimney and ignited, vents being made near the top of the pile. This causes a cone, with the apex downwards, of the pile to be charred, and, by opening vents lower down, the angle of the cone is enlarged. This process is continued until the base is reached. When the smoke issuing from the pile is seen, by its blue colour, to be free from aqueous vapour, the charring is complete. The charcoal is then drawn from the bottom of the pile, and in small quantities quenched with water or dust. Small piles are carbonised in six to fourteen days; but if the diameter be more than 30 feet, the process occupies a month.

Logs as much as 24 feet in length may be charred in rectangular piles. They are laid together in the form of a wedge, of which the breadth is limited by the length of the logs. The heap is 20 to 30 feet long, and 7 to 9 feet high at the upper end, and only 3 feet high at the lower end. It is surrounded on all sides with a layer of sods and charcoal dust, and by a wooden covering supported by vertical stakes. On the top is placed a

<sup>1</sup> On charcoal-burning, consult G. Svedelius' *Handbook for Charcoal Burners*, translated from the Swedish by R. B. Anderson and W. J. L. Nicodemus (New York, 1875).



roof of twigs, leaves, and charcoal dust. At the lower end a horizontal chimney is left. Vents are opened at the opposite end so as to give planes of charring. Rectangular piles are used in Sweden and in Austria. In China the carbonisation is effected in pits provided with a chimney communicating with the bottom.

Experiments, on a large scale, on the amount of charcoal yielded gave the following results:—In France, with circular piles of 2120 to 3180 cubic feet, the yield by weight was 17 to 21·3 per cent.; in Belgium, on charring wood fifteen to twenty years old, half hard, half soft, the yield at the ordinary rate was 15 to 17 per cent., but when charred more slowly, 20 to 22 per cent.; in Sweden, from pine wood, the yield was 20 to 28 per cent. By volume, the yield of charcoal varies from 50 to 75 per cent.

By using closed ovens the yield of charcoal may be somewhat increased, and valuable by-products obtained from the gases, which may afterwards be used for heating the ovens. Peat may be charred, like wood, in heaps or in kilns. Peat-charcoal, however, on account of its lightness, friability, and its high percentage of ash, is not adapted for metallurgical purposes, and its application has not advanced beyond the experimental stage.

(b) **Coke.**—Coke is the carbonaceous residue from the dry distillation of coal. Good coke should possess sufficient strength to withstand the pressure in a blast furnace without crushing. For this reason only those coals which give on dry distillation a coherent residue can advantageously be used. The coals of the second, third, and fourth groups of Gruner's classification are suitable for coking. A high percentage of ash has a detrimental influence on the coke produced, and must therefore be removed by subjecting the coal to a preliminary washing.

Coke varies considerably in its external characters. It may be porous and light, or compact and heavy; black and dull, or light grey and bright, with a semi-metallic lustre. The porosity of coke induces a tendency to absorb gas. Like charcoal, coke is hygroscopic, absorbing 1 to 2·5 per cent. of water from air at the ordinary temperature. When dipped in water, coke will absorb 20 to 50 per cent. The calorific power of coke, free from ash, is 8000, or nearly that of pure carbon.

The earliest method of preparing coke was by carbonising coal in the open air in heaps without any external covering. A more economical method is by carbonising the coal in mounds, piled round a central octagonal chimney. The mound is ignited at the top, and the operation proceeds exactly as in charcoal-burning. The mounds are usually 12 to 21 feet in diameter and 9 to 15 feet high. The yield after five days' coking is 65 per cent. of the theoretical quantity.

In Upper Silesia, rectangular kilns have been used for coking for many years. They are cheap, easy to work, and give a large output, but, like the mounds, they do not yield a uniformly coked

product. They are chiefly used for coking coal slack. These kilns, or Schaumburg coke-ovens, fig. 122, have two fixed parallel walls 18 yards long and 5 feet high. The walls are 8 feet apart, and are provided with a series of square openings 2 feet apart and 1 foot above the sole, the apertures, *c*, in one wall being opposite those in the other. From each aperture ascends a vertical flue, *d*, which may be closed with a tile. In order to charge the kiln one of the open ends is bricked up, and moistened coal slack is stamped in up to the level of the apertures. From the apertures in one wall wood stakes are placed across, the ends passing into the corresponding apertures on the opposite side, and the whole kiln is filled with moistened slack and covered with loam. On withdrawing the stakes, the passages formed communicate with the horizontal apertures and with the vertical flues in the side walls. The process consists merely in starting the combustion and regulating the air current in the flues, and is complete in

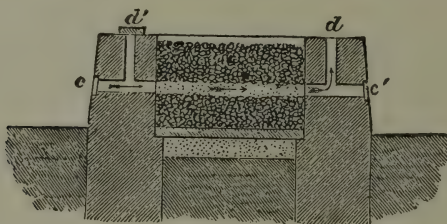


FIG. 122.

about six days. The flues are then closed, and the coke, after cooling for two days, is withdrawn at the open end.

These wasteful methods of coking are now generally superseded by coking in ovens of brick or stone, in which carbonisation is effected mainly by the heat resulting from the combustion of the volatile products evolved during the process, the aim of the coke-burner being to bring air into contact with these gases, but to prevent its contact with the coke formed.

The coke-ovens that have been introduced to obviate the loss of heat occurring in heaps and kilns are of very various types. The simplest form resembles a beehive or a baker's oven. This is a sort of covered-in mound or meiler. It is lined with fire-bricks, and air is admitted through a doorway closed with loosely piled up fire-bricks. There is thus, as in cases of the mound and kiln, partial combustion in the coking space itself, and so some coke is burnt. The cavity of the oven is 6 to 12 feet in diameter and  $4\frac{1}{2}$  to 9 feet in height. The doorway is about  $2\frac{1}{2}$  feet square, and the coke is drawn through it and quenched in the open air. In some cases the coke is cooled in the ovens before it is drawn, by watering it by means of a hose. This quenching, by

double decomposition, removes some of the sulphur from the coke in the form of sulphuretted hydrogen. Sometimes the ovens have the form of a rectangular chamber 10 feet deep, 12 feet wide, and 10 feet high. The working of the ovens is very simple. On the base, heated from the last charge, or on a layer of slack, the coal ( $1\frac{1}{2}$  to  $4\frac{1}{2}$  tons) is charged in. The door is then closed and carbonisation commenced. If the oven is cold, before shutting the door, fire is introduced, and the lower holes in the doorway are left open. The coking proceeds from the top downwards, the draught-holes being successively

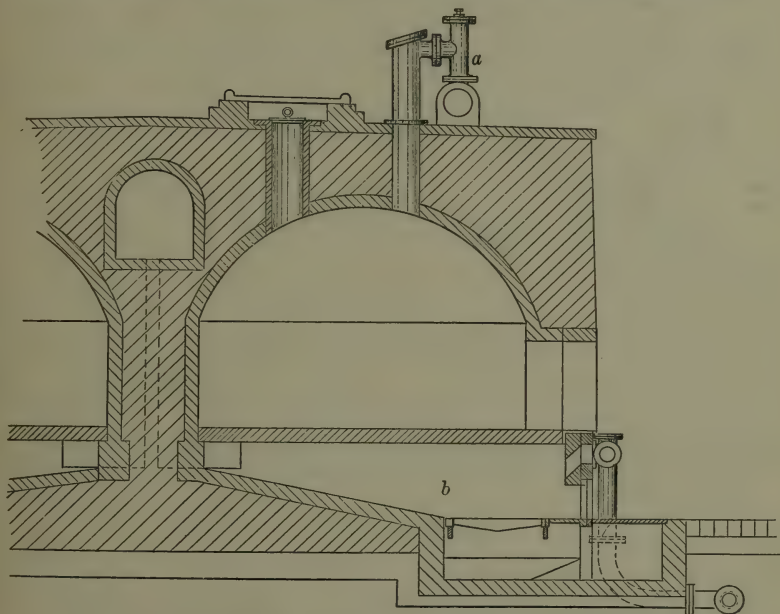


FIG. 123.—Pernolet Coke-oven. *a*, gas outlet; *b*, bottom firing flue.

stopped as the level of the carbonisation sinks. The coking lasts from seventy-two to ninety-six hours, and the coke is often left in a further ten or twelve hours before being drawn.

Of modified beehive ovens, designed with a view to effecting a saving of by-products, the three following have received some recognition.

The Pernolet coke-oven (fig. 123) differs but little from the ordinary beehive, but it has a fireplace and grate, and the gas is carried into the upper collecting-tube, *a*, and returned to the bottom flue, *b*, where it is fired with solid fuel.

At the Almond Ironworks, Falkirk, Mr H. Aitken<sup>1</sup> adapted

<sup>1</sup> *Trans. N. Eng. Inst. M.E.*, vol. xxix. (1879).



means for the recovery of by-products to the beehive oven. The Aitken coke-oven, as shown in fig. 124, is a beehive oven fitted with two pipes,  $a a'$ , for conveying the blast and gas from the condensers through small openings in the roof distributed equally round the circumference, whilst channels,  $b b' b''$ , in the floor of the oven conduct the collected by-products to an external pipe,  $c$ , which leads them to the condensers. The main body of the oven measures 5 feet from the opening in the roof for filling in coal to the floor, and has a diameter of 9 feet.

The Jameson coke-oven<sup>1</sup> is another improvement on the beehive oven. It is shown in cross section and in sectional plan in fig. 125. In the bottom of the ordinary beehive oven,  $a$ , channels are formed, covered with perforated tiles,  $b b' b''$ , connected out-

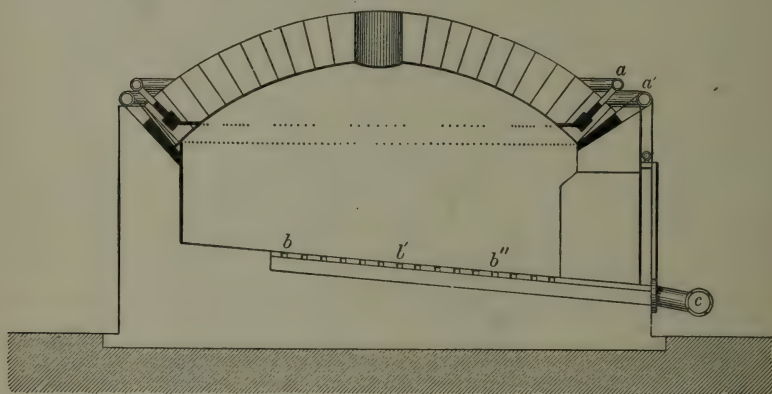


FIG. 124.—Aitken Coke-oven.  $a a'$ , gas and air inlets;  $b b' b''$ , by-product collectors;  $c$ , gas and by-product pipe to condensers.

side the oven with pipes leading to apparatus,  $C C'$ , for producing a slight suction, and for discharging the by-products when required. The cost of applying this process is small, and the results of a series of trials show that the average yield of coke is 65·49 per cent., the average yield of ammonium sulphate and of oil being 4·6 lbs. and 6·1 lbs. per ton respectively.

The use of beehive and modified beehive ovens is now, however, somewhat limited. The waste entailed by employing the beehive oven prohibits its use, except for small quantities of coke or for special purposes; whereas, if any attempt is made to recover the products of distillation, the usual practice is now to adopt one of the more modern ovens.

In the improved forms of coke-ovens air is not admitted into the coking space, but into side flues, so as to mix with the

<sup>1</sup> *Journ. Soc. Chem. Ind.*, vol. ii. (1883), p. 114; *Journ. Iron and Steel Inst.*, 1883, p. 504.



gaseous products passing through openings in the oven walls into the side flues. In this way use is made of the heat afforded by the ignited gases, which are, in the older forms of oven, allowed to pass directly into the chimney or into the open air; there is complete combustion of all the gaseous products, and the ovens are heated without any coke being actually burnt.

All ovens for coking without access of air have a rectangular

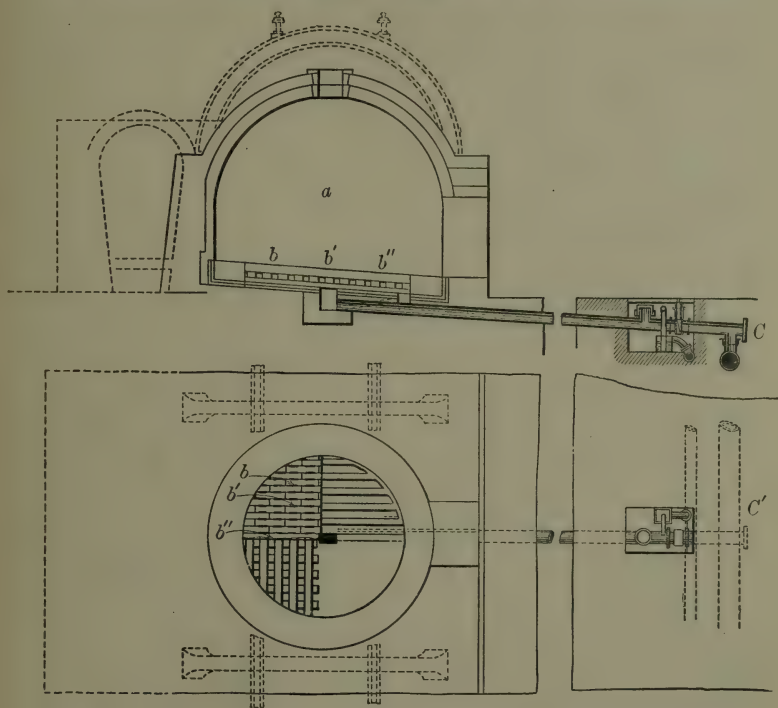


FIG. 125.—Jameson Coke-oven. *a*, coking chamber; *b b' b''*, perforated tiles; *C C'*, suction apparatus.

section, and in most cases the major axis is horizontal. The Appolt oven, however, is an exception, its principal axis being vertical. It was invented in 1856 by the brothers Appolt,<sup>1</sup> and consists of twelve or more vertical coking chambers of brickwork, arranged in rows, the series being surrounded by walls of brickwork. The ovens are rectangular in plan; they are tapered, measuring, at Saarbrücken, 4 feet 1 inch by 1 foot 7 inches at the lower, and 3 feet 8 inches by 1 foot 2 inches at the upper end, and 16 feet in height. Each oven is surrounded by an air

<sup>1</sup> *Annales des Mines*, 5th Series, vol. xiii. (1858), p. 417.

space 10 inches in width, and is provided above with a lid, and below with a door opening downwards into a vault where the coke may be received in an iron waggon. As the charging is also effected by waggons on the top of the furnace, the working is extremely simple. The brickwork of the ovens is separated by air spaces which communicate with one another and with the interior of the ovens themselves. The products of combustion are carried off to the chimney by means of flues, which have fire-brick dampers for regulating the draught, and in which there are openings to allow of their being cleaned out. The gases from the coal pass into the air spaces surrounding the retort, where they mix with air introduced through flues in the wide sides of the ovens. As in all coke-ovens, the process is conducted by first heating the ovens to redness. They are then filled, and the process may be carried on uninterruptedly. The charge in each chamber is 1 ton 4 cwt. to 1 ton 8 cwt., so that the whole oven cokes about 17 tons of coal in twenty-four hours, the work being so arranged that one retort is discharged and recharged every hour. The Appolt coke-oven presents the advantage of a very great heating surface in proportion to its capacity, which is easily explained by the fact that each chamber is completely surrounded, with the exception of the two end planes, by fire. Thus much less heat is lost by cooling from without. Dürre estimates the internal area of the walls at 50 to 58 square feet per cubic yard of capacity, and Kerpely states that the heating surface is more than 1 square foot per 20·5 lbs. of charge. The average yield of coke is 70 to 80 per cent. with caking coal, and very good results have been obtained with a mixture of caking and non-caking coals. The vertical position of the compartments presents the advantages of occupying less space than other ovens; the coke in dropping down exerts no injurious amount of wear on the sides, and the pressure of the column of coal produces a coke of greater density than that obtained in other ovens. On the other hand, the Appolt coke-oven has the disadvantage of high initial cost, and repairs are effected with much difficulty.

Numerous varieties of ovens with horizontal axes have been introduced, and worked with more or less success. In all these ovens the object sought is to utilise the gases to the highest possible degree by effecting the coking by their combustion. At first this led to the adoption of complicated constructions, which have recently been greatly simplified, and the main differences in the system of heating and in the arrangement of flues depend on whether the heating flues are horizontal or vertical in position. This naturally divides ovens into two classes.

To the class of ovens having horizontal flues belong, among others, the Simon-Carvès,<sup>1</sup> Semet-Solvay, and Hüssener; while to

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1883, p. 494; 1885, p. 108.

the class having vertical flues belong the Coppée, Otto-Hoffman, Otto-Hilgenstock, von Bauer, Brunck, and others.

The Simon-Carvès oven resulted from the investigations of Carvès and Henry Simon. The former studied the regulation and distribution of the temperature in coke-ovens by burning the waste gases in flues around the coking chamber, and found that with the coal he had to do with—a poor, non-caking coal—a high temperature rapidly and evenly distributed throughout the coal in conjunction with closed carbonising chambers were the conditions for obtaining good coke, and at the same time a good yield of ammonia and tar rich in aromatic substances.<sup>1</sup> He improved the arrangement of the horizontal side flues in which the washed gases were burnt to heat the coking chamber, and insisted on the narrow chamber to ensure the desirable rapidity of carbonisation. Simon introduced his arrangement, in which, by allowing the air for combustion, on its way to the oven, to pass through passages running between the underground waste gas mains, the heat from these gases passed to the air, which became heated. In the early form of oven the residual gases, returned from the washers, were burnt over a solid fuel fire on a grate built for the purpose in the lower part of the walls separating the coking chambers. The heated and burning gases then circulated in two side flues, ascended to the uppermost of the three horizontal flues in the wall, and thence descended these in succession on their way to the waste flue leading to the chimney.

In the later forms of this oven the grate and fireplace are dispensed with, the heat for the coking being derived wholly from the combustion of the gases, air being admitted under pressure to support the combustion.

The construction of a modern Simon-Carvès oven is shown in fig. 126. There are charging holes,  $aa'$ , in the top of the oven, and the gases are drawn off through a pipe,  $bb'$ , which is provided with a regulating valve. From here the gases pass into a system of pipes common to 30–50 ovens, and kept cool by jets of water, so that the tar and ammoniacal liquors are condensed. The lower open ends of the pipes dip into a collector for the products of condensation, similar to that employed in many gas-works. The gases from the condenser are then passed through scrubbers filled with moistened coke, where the last traces of ammonia are removed. The uncondensed gases pass onwards to the oven for heating purposes, entering through an aperture,  $c$ , in the basal flue of the oven, whilst the air for combustion enters at several points as shown in the figure. Under the base of the oven the burning gases pass, then rise between two adjacent ovens to the bottom one of the side flues,  $e$ , and pass gradually upwards through  $e'$ ,  $e''$  and  $e'''$  to the flue, which conveys them

<sup>1</sup> These historical details are copied from a paper by D. A. Louis, *Journ. Iron and Steel Inst.*, 1903, No. 2, p. 293.



to the chimney or under steam boilers. The ovens are 30 feet long, 2 feet broad, and  $6\frac{1}{2}$  feet high. The yield is about 75 per cent. The coke produced possesses sufficient resistance to render it suitable for blast-furnace use.

The air introduced receives a previous heating to some  $500^{\circ}$  or  $600^{\circ}$  by its being brought into contact with the hot flues conveying away the spent fire-gases from the ovens. At the part of the bottom flue where the greatest heat is sustained, the walls are lined with the best silica bricks. The heated air admitted into the bottom flue is purposely insufficient for complete combustion of the gas introduced there, the further supply of hot air being admitted into the side flues of the oven. The arrangement

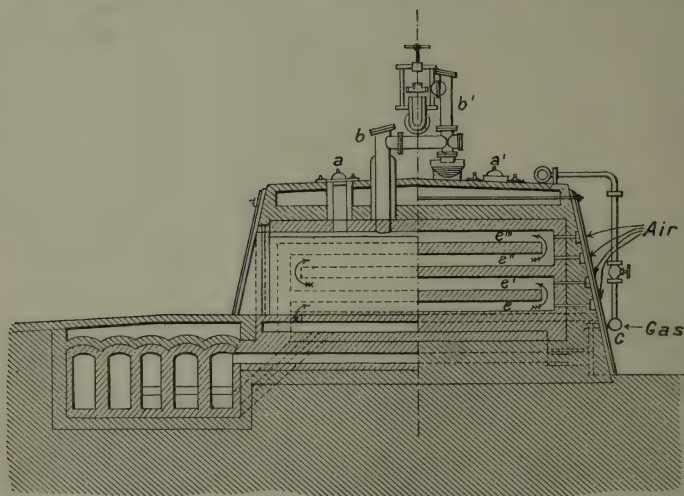


FIG. 126.—Simon-Carvès Coke-oven.  $aa'$ , charging-hoppers;  $bb'$ , gas outlet;  $cc'e'e''e'''$ , combustion flues.

for thus admitting the air is completely controlled by dampers. Each oven is charged with  $4\frac{1}{2}$  tons of coal, the time for coking being a little over forty-eight hours.

After coking is complete, the product is discharged by means of a ram carried on a truck which runs on rails behind the ovens; this ram is introduced at the end of the oven with the smaller sectional area, and as the coke emerges from the larger end it is quenched with water. The ram is propelled by a cogged driving-wheel, worked by a small portable engine.

The Semet-Solvay oven (figs. 127, 128) has horizontal flues on the Carvès principle, but instead of the flues constituting the wall between two ovens this is made solid, and the flues are composed of hollow tiles on either side of it. This renders the



flues of each oven independent of adjoining ovens; and since the weight is entirely borne by the solid walls between the ovens, these flues can be made much thinner, and consequently more efficient.

In this case only so much pre-heating of the air takes place as is acquired during the passage of the air through cooling flues in the structure, and great care is taken to equally distribute the heat in the flues. For this latter purpose part of the gas and air enter the uppermost flue in the front of the ovens; more gas is admitted from the back of the ovens into the middle horizontal flue, whilst still more is admitted into the lowest flue from the front.

The coal is charged in through hoppers in the roof, and the coke is discharged in exactly the same manner as is used in the Simon-Carvès oven.

The Hüssener<sup>1</sup> oven was introduced into this country from Germany in 1901, a plant of 60 ovens being built at the Clarence Works, a further 60 being added in 1904. This oven resembles the Semet-Solvay in several particulars; for

instance, in both ovens there is a solid brick wall between each coking chamber which carries the top arch of the oven and the

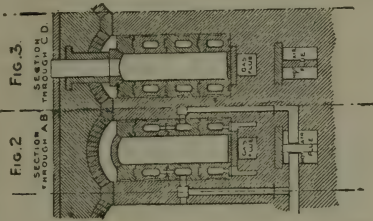


Fig. 127.

Semet-Solvay Coke-oven.

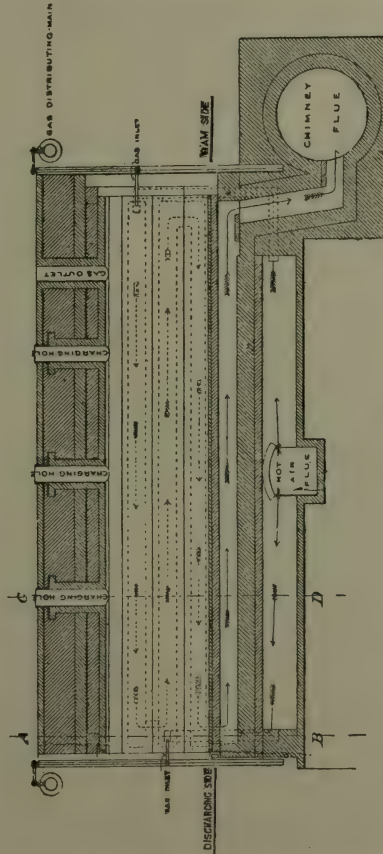


Fig. 128.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1904, No. 1, p. 188.

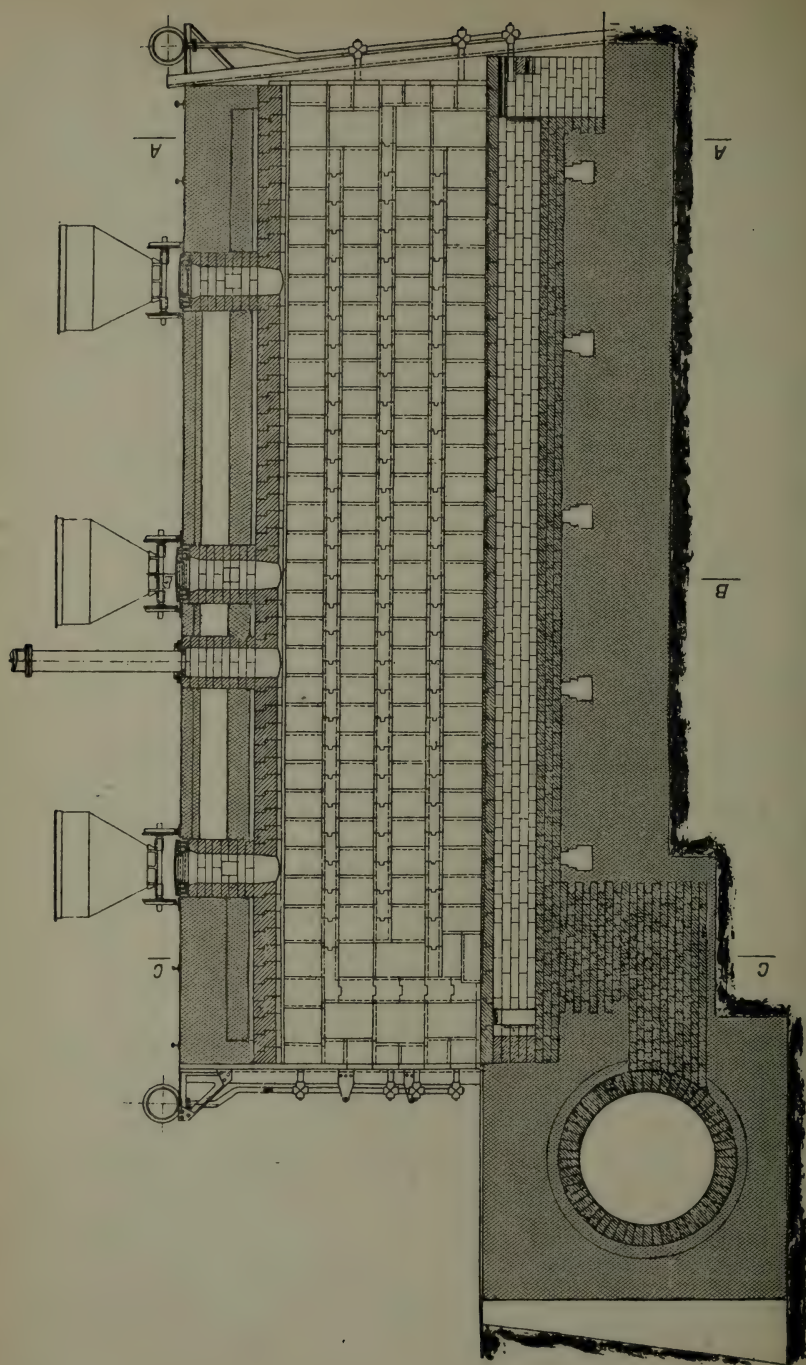
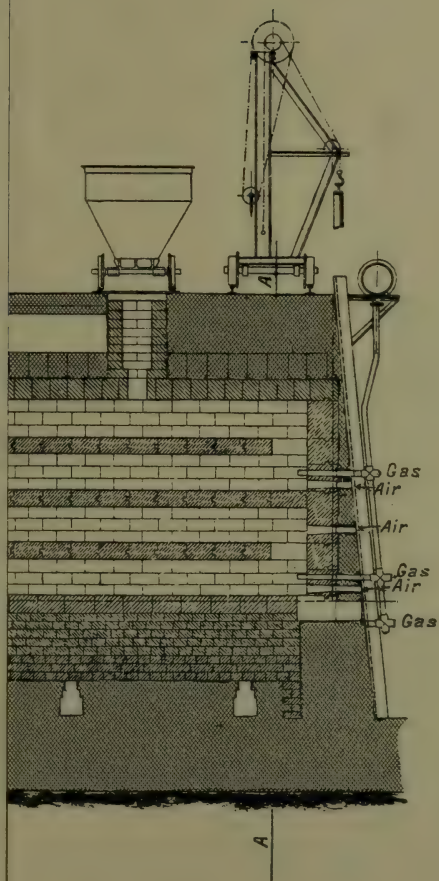


FIG. 129.—Hüssener Coke-oven. Section D D through coking chamber.

[To face p. 268.



es.





superstructure, leaving little or nothing to be carried by the side walls of the coking chamber, which can consequently be made much thinner than usual, and so allow the heat to pass more rapidly through them with less consumption of gas. This arrangement also permits any single oven to be laid off for repairs without interfering with the working of its neighbours, and also allows the vertical walls of the oven to be removed and rebuilt without disturbing the top of the oven in any way. The construction of the oven is shown in figs. 129, 130, and 131; fig. 129 being a horizontal section through the coking chamber, fig. 130 a horizontal section through the heating flues, and fig. 131 containing three vertical sections at A, B, and C.

The coking chambers are about 33 feet long, 7 feet high to the crown of the roof, and are slightly tapered to assist the removal of the coke by means of a ram, being 1 foot 6 inches wide at the narrow or ram end, and 1 foot 9 inches wide at the wide or quenching end. Each oven is fitted with three charging holes, and one opening for the removal of the gases. At the ram side the oven is fitted with ordinary fire-doors in order to get up heat on starting, and on each side of the charging holes there are two loose bricks (marked *a* and *b* in the section on B B, fig. 131); by taking these out, gas from the ovens is allowed to pass into the flues without going through the washing apparatus. This arrangement also permits the ovens to be used for the manufacture of coke alone without the by-products. As soon as the oven is in work, and when making by-products, these holes are permanently bricked up. In regular working, the gas coming back from the various washers, etc., enters on the ram side underneath the floor of the oven into two parallel flues, between which is a solid brick wall. Each of these flues is connected with the upper flues of the oven on the same side. The great advantage of this is that the heat can be the more easily regulated on each side of the oven. The gas, having passed through the bottom flues, rises up to the top of the oven, receiving on its upward course a second, and on turning into the top flue a third, supply of fresh gas. After passing back in the upper flue, the gas falls to the second one, being enriched by a fourth supply of gas, and then passes along the third flue, enriched as before, down into the fourth flue, where it is found unnecessary, as a rule, to add more gas, and so into the waste flue leading to the boilers and chimney.

It will be seen that the flues are in two separate divisions, each heating one half of the oven, both bottom and side. All the gas is forced to pass through every part of the flue; and as it is enriched in so many places with fresh gas, the heating of the coking chamber is very regular, and is entirely under the control of the burner. A large proportion of the air necessary to burn all the gas is admitted in the bottom flues; any further supply

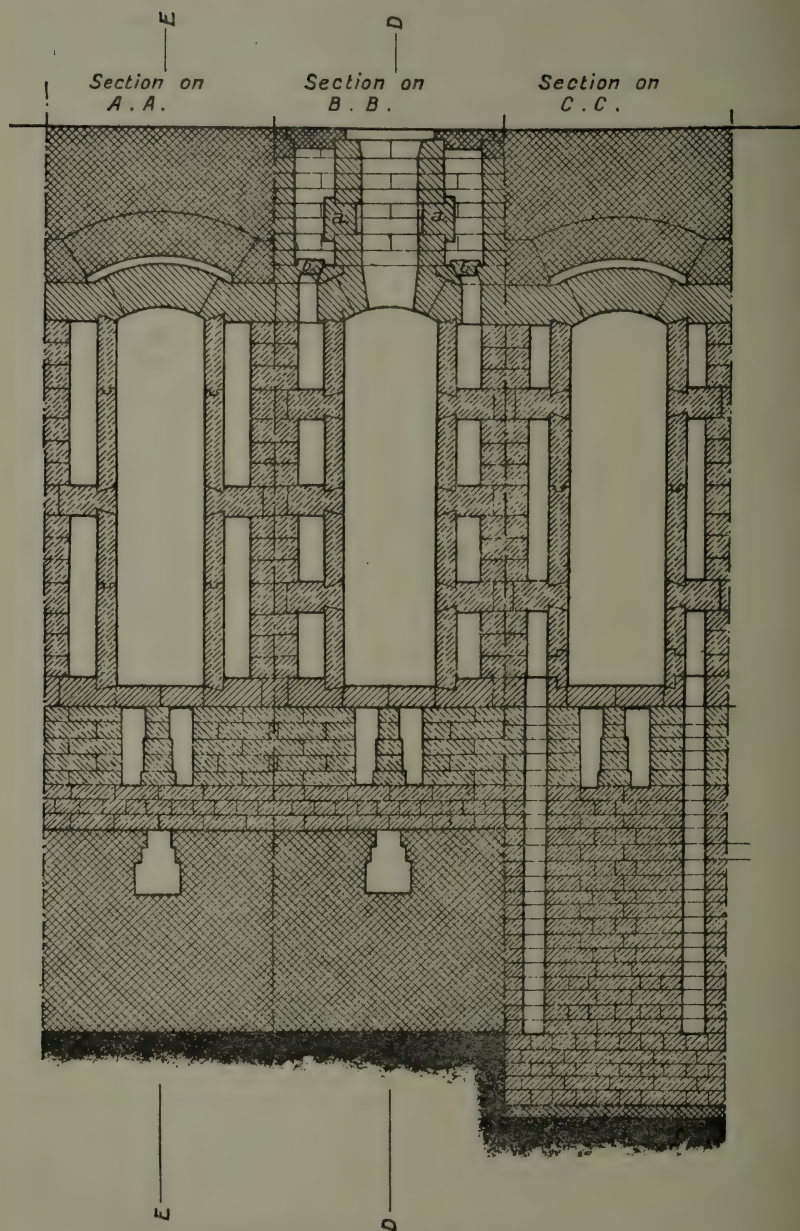


FIG. 131.—Hüssener Coke-oven. Showing vertical sections.

can easily be regulated by means of the sight-holes, which are fixed close to the inlets. About 70 per cent. of the total gas from the coking process is used in heating the ovens, and having done this, passes under the boilers at a temperature of  $825^{\circ}\text{C}.$ , raising sufficient steam for the exhausters of the ovens themselves, for the by-product plant, and for other purposes. The time required for coking is thirty-two hours, using wet coal containing 10.5 per cent. of water. The production of each oven is about 22 tons of coke per week, each charge consisting of 6.5 tons of wet coal, giving 4.36 tons of coke.

Of ovens with vertical heating flues, the Coppée was the first, and this method for distributing the heat round the coking chamber has been very largely and successfully adopted in modern ovens. The Coppée ovens are usually built in series of thirty or forty, and are worked in pairs. The ovens, which are 30 feet long, 18 inches wide, and 4 feet high, have each twenty-eight vertical flues leading from the top through the partition-wall common to two ovens, to the horizontal flues that pass underneath the chambers in the direction of their length. In these horizontal flues the gases from a freshly charged oven mix with those from one in which the coking is nearly complete, and combustion is effected by air admitted through three small openings. At each end of an oven are two metal doors. The coke is removed from the oven by means of a ram, as previously described. When the coking is complete, the engine and ram are placed opposite the end of the oven, and the coke is pushed out, the operation lasting about two minutes. A jet of water is then applied to the coke. At the same time the lower doors of the oven are closed, and coal is fed in through three openings in the roof, the openings being then covered by sliding doors. The coal is then levelled by means of rakes, and the upper doors are closed. The whole operation, from the opening to the closing of the doors, lasts only eight minutes. When working thirty of these ovens, numbered consecutively, those with odd numbers are drawn in the morning, and those with even numbers twelve hours later, the coking occupying twenty-four hours.

The various Otto ovens belong to the vertical flue group, and have shown a gradual change in construction and method of regulating the heat of the chambers. In the earlier forms of Otto-Hoffman ovens both the gas and air necessary for the combustion were pre-heated before being used, but in the later forms the air only is pre-heated.

The Otto-Hoffman<sup>1</sup> oven itself has undergone some modification, for the earlier forms were encumbered underneath with regenerating checkerwork chambers, which alternately conducted the heated waste gases away from, and the air supply to, the ovens. Later on, the regenerators were put under the ends of

<sup>1</sup> See D. A. Louis, *Journ. Iron and Steel Inst.*, 1903, No. 2, p. 293.



the ovens, there being regenerators at each end, and connection with them was made through the flue beneath the coking chambers, which was divided transversely across at the middle. In working this form of oven, gas and then heated air were admitted at one end of the sole flue; combustion immediately ensued, and the burning gases passed up the flues on one side into the upper flue, and then down the vertical flues on the other side of the central division, along the other half of the sole flue, to the regenerative chamber. In a further stage of development, the regenerators were reduced considerably in size, and placed underground in front of the ends of the ovens, leaving the arches under the ovens entirely unencumbered; moreover, the gas was supplied at the top as well as the bottom, so distributing the area of combustion. A further modification has now been adopted, the Hoffman element—the regenerator—being dispensed with, and the gases for combustion, instead of being admitted unburnt into the flues, are led by piping beneath the wall between each oven, and from Bunsen jets rising from the piping are burnt in orifices opening into the side horizontal bottom flue, and rise through the vertical flues to the horizontal top flue, whence they descend a narrow vertical flue at the end leading to a flue under the bottom of the coking chamber, along which they sweep, ultimately passing as waste gases through an opening, controlled by a damper, into the waste gas main. The Otto-Hilgenstock coke oven, which is shown in fig. 132, illustrates this modification.

The standard oven is 33 feet 7 inches long, 6 feet 6 inches high, and 1 foot 9 inches wide at the middle. The gases given off from the coal in the oven chamber A pass through the opening B into the gas main C, whence they are drawn to the by-product plant by means of exhaust fans. The washed gases are returned by the main D, and from this main pipe a number of smaller pipes E branch out into the arches which support the ovens, and from these smaller pipes are led lateral branches which rise up to nozzles to which Bunsen burners are fitted, and by their action sufficient air is drawn in for combustion, this air being sufficiently heated on its way through the arches of the ovens. The flame rises vertically into the horizontal bottom flue, and ascends through the vertical heating flues F into the horizontal top flue G. From this flue the gases are led into the centre through the vertical flues H, under the bottom of the oven I, through opening K, to waste gas main M, thence to the boilers and chimney.

The Brunck<sup>1</sup> ovens resemble others in having long chambers supported on a substructure, but this substructure is of some complexity, as it contains an elaborate series of connecting ducts, cooling channels, checkerwork chambers, and vaulted conduits. These arrangements serve for the removal of the waste gases and for pre-heating the air supplied for combustion, as well as for con-

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1903, No. 2, p. 298.



ducting it to the points where it is required. Again, to ensure a

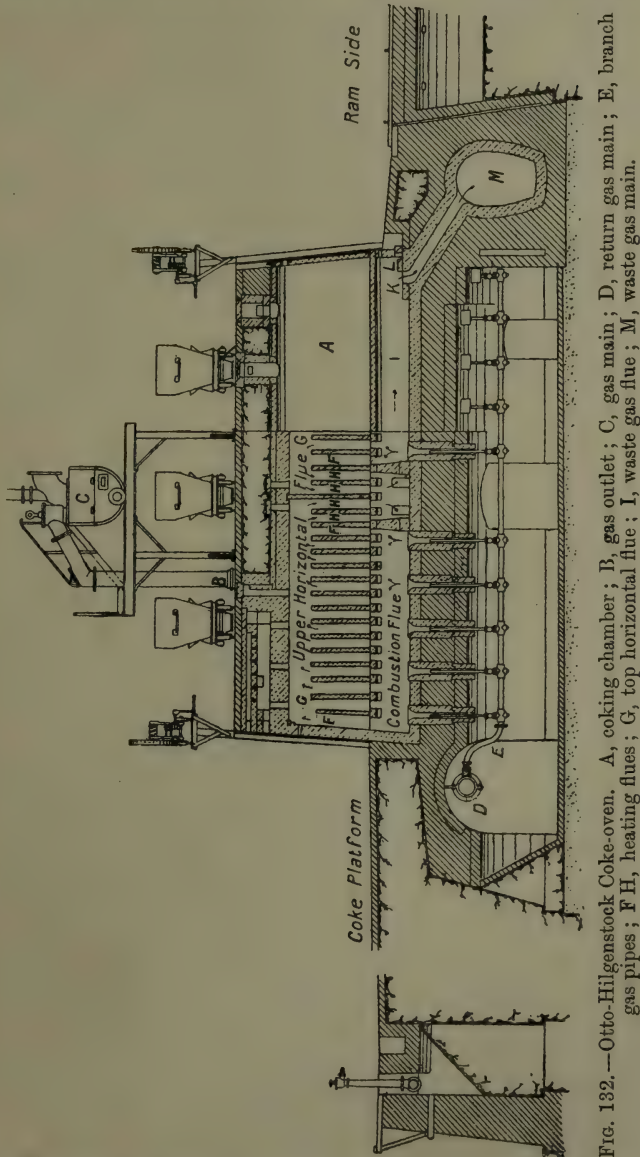


FIG. 132.—Otto-Hilgenstock Coke-oven. A, coking chamber; B, gas outlet; C, gas main; D, return gas main; E, branch gas pipes; F H, heating flues; G, top horizontal flue; I, waste gas flue; M, waste gas main.

better distribution of the heat, the ovens are heated from each end independently; hence all the substructural arrangements are

in duplicate. The coking chambers are built on the top of an upper row of cooling passages, arched chambers being first constructed, separated by solid walls, and within these the coking chambers proper are built, with a longitudinal flue below each one, whilst vertical flues, arranged on each side of each chamber, connect this lower longitudinal flue with a longitudinal flue above. The lower flue is divided into four sections by parting-walls, and a parting-wall extends all round the outside of the coking chamber at the centre, completely shutting off one side of the heating spaces from the other.

The firing of the ovens is effected by six gas-jets, three at each end, of which one is set in the sole flue and one in each side, while the air forced along by a fan traverses various passages below, and is delivered by ducts and ports to the scene of action. The burning gases ascend the end flues and descend the flues at the centre, passing into the waste mains which run below the

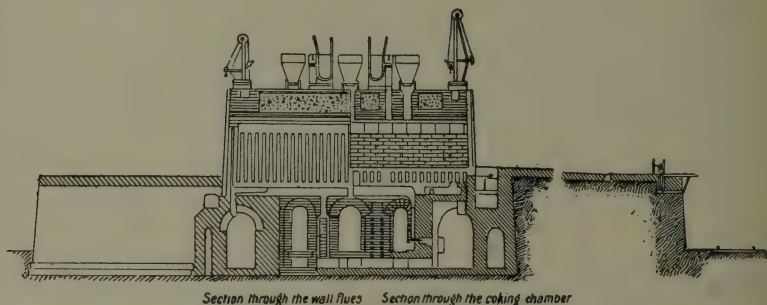


FIG. 133.—Brunck Coke-oven.

centre, and at right angles to the direction of the ovens. There are two of these mains, and between them is built the two sets of checkerwork, through which part of the air supply passes on its way to the combustion chamber and becomes highly heated. The rest of the air supply passes through a special conduit and through various cooling passages, taking up heat on the way.

Further, the air supply is used to cool the products of distillation, and thus takes back to the ovens some of the heat that would otherwise be wasted, and in addition economises water required for cooling. The Brunck oven is built  $33\frac{2}{3}$  feet long, from 6 feet  $6\frac{3}{4}$  inches to 7 feet  $4\frac{3}{4}$  inches in height, and from about 17 to 22 inches in width, and has a capacity of from 5 to  $7\frac{1}{2}$  tons of coal, containing from 10 to 15 per cent. of water. Figs. 133, 134, and 135 illustrate the design of the Brunck system.

Fig. 133 is a longitudinal section partly through the wall flues and partly through the coking chamber; below the latter is shown the lower longitudinal flue, with the openings into the side

flues; beneath these are shown the air-admission flue, cooling passages, and checkerwork. In this figure are also shown three filling trucks and openings, gas take-off, and winches for lifting doors, etc. Fig. 134 illustrates various cross sections and elevations, and the special features of the substructure are set forth. Fig. 135 is a sketch of the path traversed by the gases and the

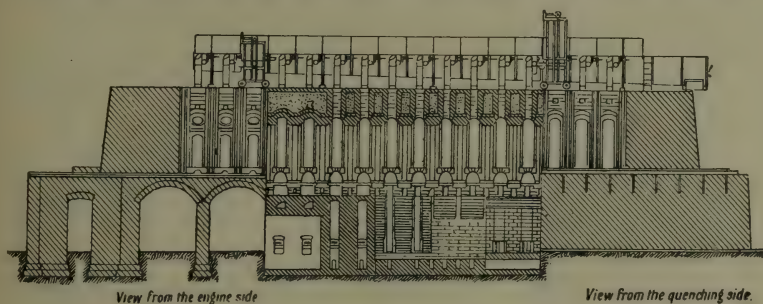


FIG. 134.—Brunck Coke-oven. Cross section.

simultaneous pre-heating of the air, showing the by-product recovery plant.

The von Bauer<sup>1</sup> oven resembles the Brunck oven in one particular, that is, in having the heating system of one end separated by a parting-wall from the heating system at the other end.

The von Bauer oven has a simple vaulted substructure with a

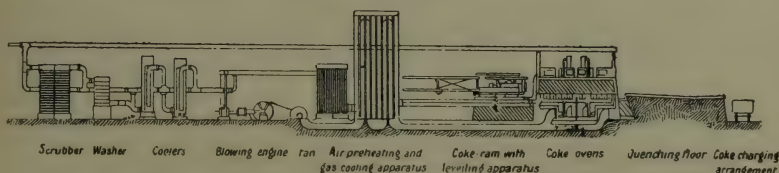


FIG. 135.—Sketch of the path traversed by the gases of a coking installation with the recovery of by-products of the Brunck system.

simple set of alternately wide and narrow longitudinal cooling channels, separated by thick walls, but connected by transverse ducts. Upon these walls are built the walls of the coking chambers, which are constructed with three sets of vertical flues or passages, the outer ones serving for combustion chambers, the central set for the air supply; under the coking chamber and over the wider cooling channels there is the usual longitudinal vaulted combustion chamber (G, fig. 136), but divided transversely by a wall at the centre, and it only connects with the group of

<sup>1</sup> D. A. Louis, *Journ. Iron and Steel Inst.*, 1903, No. 2, p. 300.

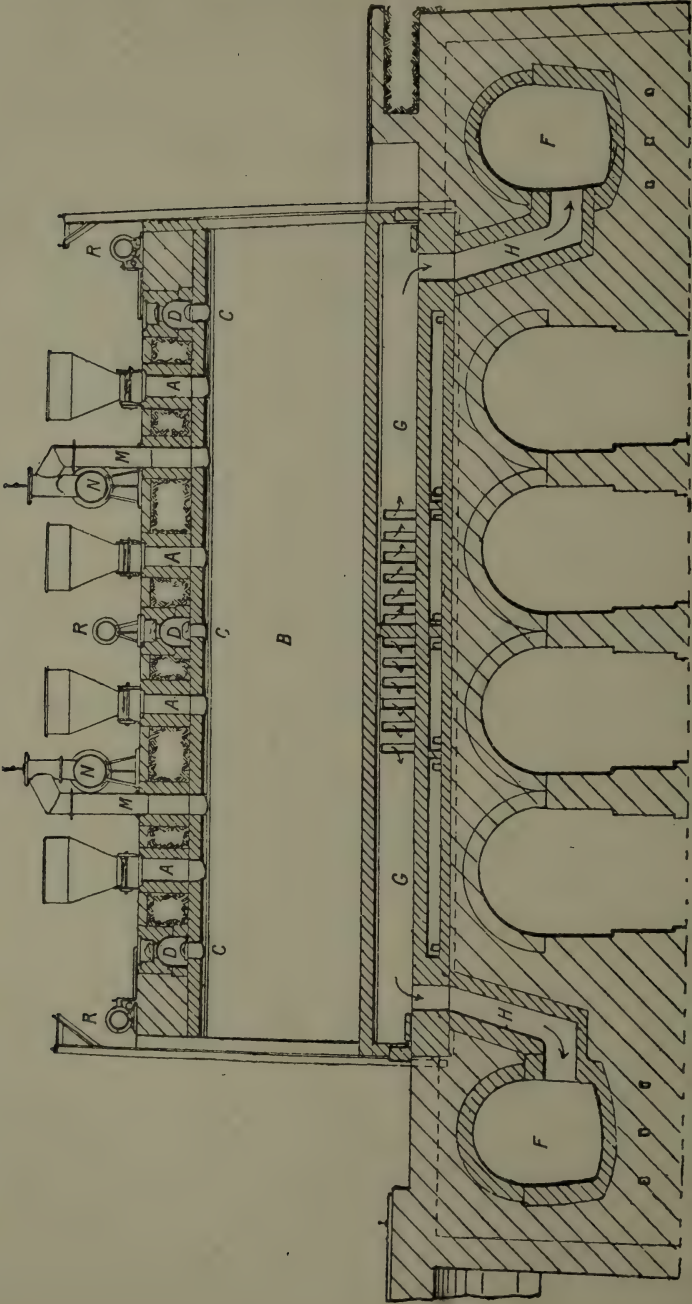


FIG. 136.—Von Bauer Coke-oven. Section through coking chamber, B; A A A, charging openings; M M, gas outlets; G G, combustion chamber; H H, waste gas flue; F F, waste gas mains.



side flues near the centre, there being no connection between this bottom chamber and the three groups of flues nearer the ends. This chamber, however, is in direct communication with the waste gas main at either end (H H, fig. 136). The air passages communicate with the combustion flues in such a manner that air is admitted exactly where required. The combustion flues unite in an upper longitudinal flue, divided into two portions by a central wall, and each of these portions is further subdivided into two groups of four flues and a larger central group of eleven flues (fig. 137). There is also a lower longitudinal flue, in which the first eight flues and the first five central flues unite, all the other flues being separated by walls from one another, and it is at these points that the six central flues on each side of the middle wall connect with the chamber under the coking oven.

Each group of flues receives its own supply of air, which is delivered at the desired spot to properly assist combustion, but before entering the combustion flues it traverses either the cooling channels below, or, when entering from above, some length of the air flue, and so becomes heated. It is, however, the upper part of the oven which differs essentially from ovens previously described. The roof of the oven is pierced by nine openings (fig. 136); four of these are spaced at equal intervals, and serve for charging the ovens when loose coal is used, the charging taking place through the end door when compressed coal is used (see p. 280). Two of these openings serve for the removal of products of distillation; the remaining three are in connection with three chambers or conduits (D, fig. 137), running at right angles to the direction of the coking chambers, across the whole battery of ovens, one being at the middle, the other two near the ends. These conduits, where they pass over the combustion flues, connect with them by vertical ducts, there being a duct for each of the two end groups and for each of the six-flued central groups; moreover, by means of piping above, these conduits can be connected with the return gas from the by-product works.

These conduits serve to supply the gas, either from the coking chambers direct or from the by-product works, the gas passes into them, and through the ducts into the combustion flues, where it is burnt with the air supply, passing down the first two groups of flues into the lower longitudinal flue, where it meets a further supply of air at the bottom of the next group of flues, up which it passes into the upper longitudinal flue, where it encounters a fresh supply of gas from the duct leading from the central gas-conduit, and another supply of air at the top of the last group of flues, down which it passes into the big flue under the coking chamber, and thence into the waste main.

By this arrangement of conduits the by-products may be collected during any stage of the coking operation from any of the ovens. The von Bauer oven is built from 26 to 39 feet long,

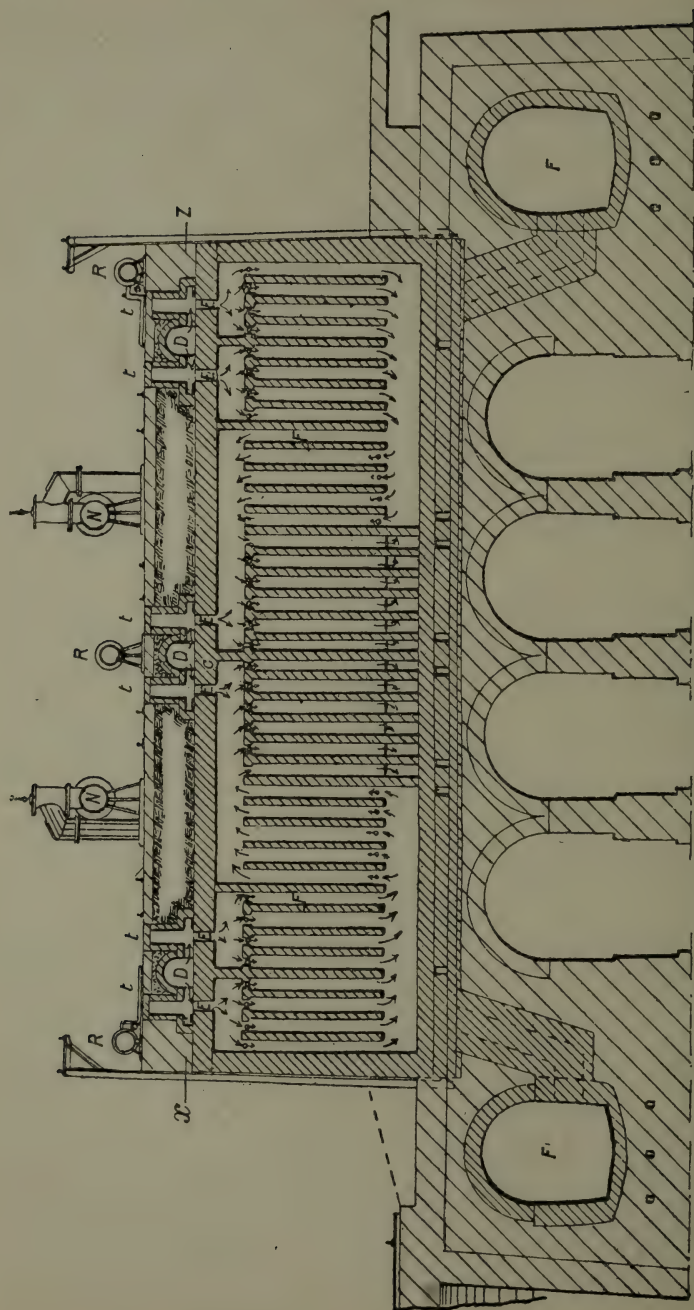


FIG. 137.—Von Bauer Coke-oven. Section through the combustion flues. R R R, gas supply; D D D, gas conduits; E E E, gas inlets.

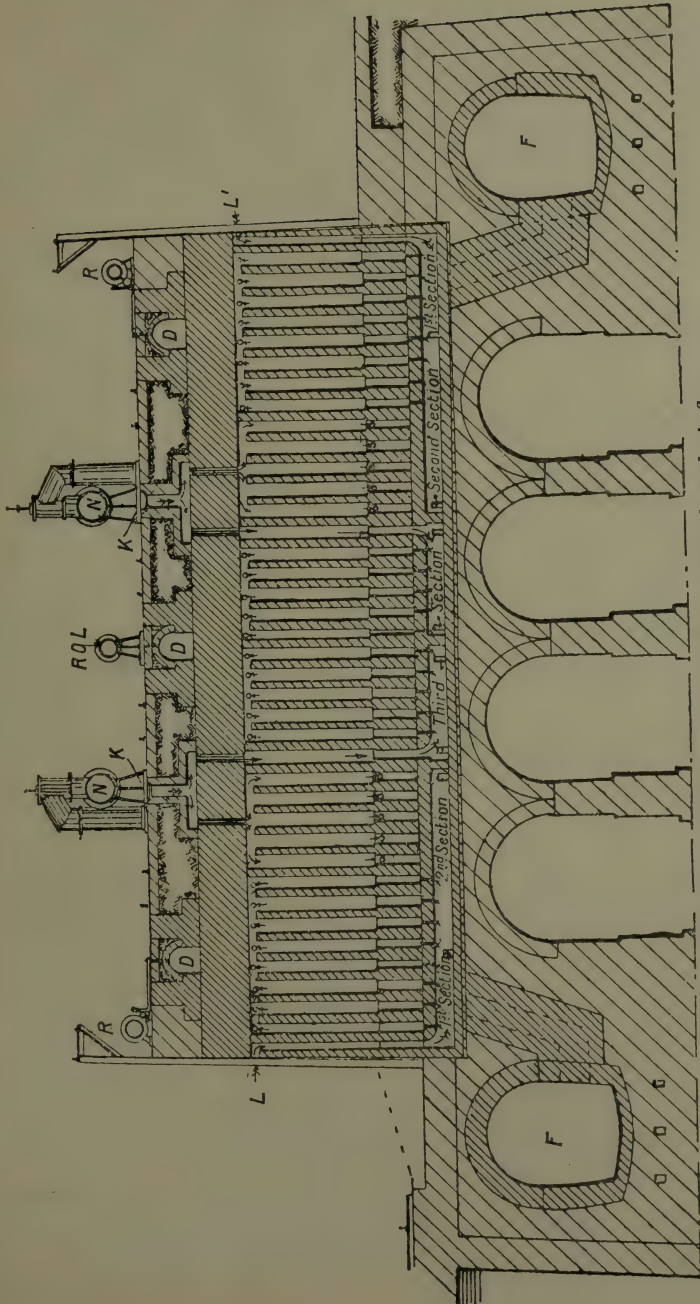


FIG. 138.—Von Bauer Coke-oven. Section through air flues.



7 feet high, and  $21\frac{1}{2}$  inches wide at one end, tapering to  $19\frac{1}{2}$  inches at the other end; the capacity of the larger being about 10 tons of loose coal, or  $12\frac{1}{2}$  tons compressed coal.

Fig. 136 is a sectional view of von Bauer's oven through the coking chamber B; fig. 137 is a longitudinal section through the combustion flues F; fig. 138 is a longitudinal section through the air flues; figs. 139 and 140 are cross sections showing the arrangements of flues, passages, and chambers.

Considerable progress has been made during the last few years in the successful coking of inferior or poorly-caking coals by compressing<sup>1</sup> the material before charging into the ovens, and it may be here stated that coals high in ash and sulphur contents are subjected to a washing process in order to eliminate a portion of

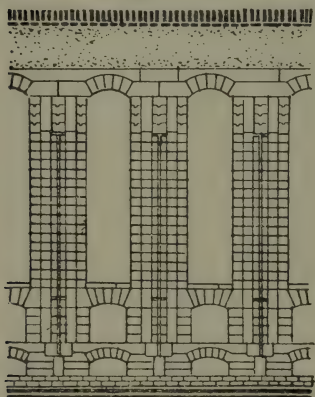


FIG. 139.—Von Baur Coke-oven.  
Cross section.

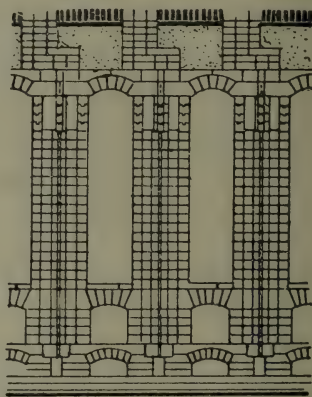


FIG. 140.—Von Baur Coke-oven.  
Cross section.

the ash and sulphur-bearing constituents. The idea of compressing fuel for coking purposes originated on the Continent, where it was observed that with coals of indifferently-caking properties the coke produced from the bottom portions of the retort ovens, compressed by the weight of the superincumbent fuel, was superior to that produced from the upper portions of the charge.

The method of compression first adopted was merely to stamp the charge in the oven by hand or by weighting the charge, and from this has gradually evolved the method now in general use of compressing the coal in a box outside the oven, the stamped cake being afterwards moved out of the box into the oven by mechanical means.

The degree to which fine coal may be compressed varies with its character, state of division, contents of moisture, etc., and the

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1902, No. 1, p. 26.



advantages to be gained by using compressed coal in coke ovens are a considerably denser coke, less breeze or small coke, quicker charging of ovens, and a diminution in the amount of hand-labour required.

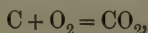
4. **Liquid Fuel.**—The prepared liquid fuels used in practical work include oils obtained by distillation of crude oils, shales, tars, and similar materials. During recent years the burners adapted for the burning of liquid fuels have been greatly improved, and very good burners have been devised for the consumption of crude tar by means of compressed air or steam.

There is little doubt that in the near future the use of liquid fuel for metallurgical purposes will be much more common than it is at the present time.

5. **Gaseous Fuel.**—The use of gaseous fuel in metallurgical operations has effected a great saving in coal. Besides this advantage, there are two circumstances that must lead to its more general adoption; these are the possibility of employing inferior fuels and waste products, and the high temperatures attainable by the use of such fuel. The method of gas-firing is, however, still far short of a universal adoption, but it may be predicted that, except in some special cases, it will gradually supersede other methods of heating.

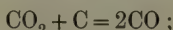
The use of gas as fuel is based on the principle that at one place all the fuel is converted into combustible gas, which is consumed by admixture with the necessary amount of air at another. These gases are produced by burning the fuel in a long column, whereby most of the carbon is burnt to carbonic oxide, whilst the hydrogen either remains free or is converted into carburetted hydrogen.

In ordinary gas-producer practice,<sup>1</sup> when a charge of bituminous coal is dropped into the producer, it first undergoes a process of destructive distillation similar to that carried out in the manufacture of coal-gas. The products of distillation are chiefly hydrogen, methane, tarry hydrocarbons, and carbonic acid, together with small quantities of ammonia, compounds of sulphur, and a large residue of coke. This incandescent coke is in turn gasified by the combined action of oxygen (air) and steam. The air is heated somewhat during its passage through the layer of hot ashes at the bottom of the producer. The process depends for its success on the chemical action of air and steam upon incandescent carbon. With regard to the method of combustion of solid carbon, the commonly accepted view has been that carbon burns directly to carbon dioxide, thus,

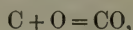


<sup>1</sup> These details are taken from the paper by Bone and Wheeler, *Journ. Iron and Steel Inst.*, 1907, No. 1, p. 126.

which reacts with the excess of incandescent carbon, forming carbon monoxide, thus,

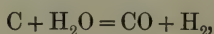


but in view of Mr H. B. Baker's work<sup>1</sup> on the combustion of solid carbon, and the work of Prof. Dixon<sup>2</sup> on the rates of explosion of cyanogen and oxygen, it is very probable that solid carbon burns directly to carbon monoxide, thus,



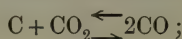
and that carbon dioxide is only formed by the secondary combustion of this monoxide. Whichever of the above views be adopted will make no difference to the thermo-chemical results obtained. When solid carbon is burnt to CO, practically 30 per cent. of its total heat of combustion is generated in the producer, and a large amount of this heat would, if not partly absorbed in decomposing steam, be lost, give rise to high temperatures in the producer, and consequently troubles with clinkers, etc.

The use of steam in the blast allows part of this heat to be utilised in doing chemical work, with the formation of hydrogen and a further quantity of carbon monoxide, according to the equation



thus raising the potential energy of the resulting gas at the expense of some of the sensible heat of the incandescent fuel.

The relative proportions of CO and CO<sub>2</sub> in the resulting gas are influenced by the reversible reaction,



and, according to Boudouard's<sup>3</sup> figures, the following mixtures of CO and CO<sub>2</sub> are in equilibrium with solid carbon, under atmospheric pressure at the temperatures given :—

Temperature.	Percentages of	
C°.	CO.	CO <sub>2</sub> .
650	39	61
800	93	7
925	96	4

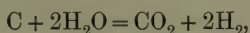
<sup>1</sup> *Journ. Chem. Soc.*, 1885, vol. xlv. p. 349; also *Phil. Trans.*, 1888, vol. clxxix. A. p. 571.

<sup>2</sup> *Journ. Chem. Soc. (Trans.)*, 1896, vol. lxix. pp. 759, 774; also *ibid.*, 1899, vol. lxxv. p. 630.

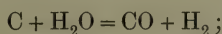
<sup>3</sup> *Annales de Chimie et de Physique*, 1901, Series vii., vol. xxiv. pp. 28-34.

From these figures it will be readily seen that when the temperature of the zone of reaction of the producer is lowered, the proportion of  $\text{CO}_2$  to  $\text{CO}$  will be increased.

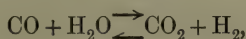
The composition of the gas obtained when steam reacts with solid carbon depends mainly upon the temperature. At comparatively low temperatures ( $500^\circ$ – $600^\circ$  C.) the chief products are  $\text{CO}_2$  and  $\text{H}$ , according to the equation



whereas at temperatures of  $1000^\circ$  and upwards the products consist for the most part of equal volumes of  $\text{CO}$  and  $\text{H}$ , according to the equation



at temperatures between  $600^\circ$  and  $1000^\circ$  the products correspond to a simultaneous occurrence of the two reactions. Both reactions are endothermic (that is, use up heat), and consequently reduce the temperature of the producer, but at the same time they raise the thermal efficiency of the gas. It must be remembered that there is also a reversible reaction represented by the equation



which may have a considerable effect on the composition of the gas. The direction in which this reaction will take place depends on the temperature of the system and on the relative masses of the reacting gases. O. Hahn<sup>1</sup> has recently determined the equilibrium ratios for varying temperatures as follows:—

Temperature. C°.	$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} = \text{K}.$	Temperature. C°.	$\frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2} = \text{K}.$
786	0.81	1086	1.95
886	1.19	1205	2.10
986	1.54	1405	2.49

From these figures it is possible to predict the direction in which any change will take place in a system containing oxides of carbon, hydrogen, and steam at any temperature, provided their relative concentrations are known. Also it is obvious that in the case of a given mixture which is in equilibrium at a low temperature, change will take place in the direction  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$  as the temperature is raised, and *vice versa*, and also that the addition of steam at any temperature will tend to cause a change in the direction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ .

<sup>1</sup> *Zeit. für Phy. Chemie*, 1903, vol. xliii. p. 705; vol. xlv. p. 513.

Bone and Wheeler<sup>1</sup> have done some very valuable work on the use of steam in producer practice, and in a series of systematic experiments they included—

1. The weighing of the whole of the coal used.
2. The continuous sampling of the gas over eight hours in the day shift.
3. The daily estimation of ammonia, tar vapour, and sulphur compounds in the gas.
4. The weekly collection and weighing of tar deposited throughout the plant.
5. The weighing of the ashes, clinker, and coke withdrawn from the bottom.
6. The estimation of soot and fine ash carried over by the gas.

The samples of coal-tar, ashes, soot, gas, etc. thus collected were afterwards analysed, and from the results the following data were obtained:—

1. The total carbon in a ton of dry coal charged into the producer.
2. The proportion of this carbon lost in the tar, ashes, and soot.
3. The proportion of the carbon actually gasified.
4. The weight of carbon in a cubic foot of the gas.
5. The yield of gas per ton of coal gasified.
6. The calorific value of the gas per cubic foot at 0° C. and 760 millimetres pressure.

From the figures actually obtained by experiment in a Mond producer, the efficiency of the producer was determined under various conditions as to the supply of steam. By efficiency should be understood the ratio of the available energy of the gas as supplied from the producer, to the energy of the coal required to produce it.

From the work mentioned the following conclusions were drawn:—

(a) *Quality and Composition of the Gas.*—The quality of the gas steadily deteriorated as the steam saturation temperature was raised beyond 65°. Thus, whereas at 60° and 65° the average percentage of combustibles exceeded 47 per cent., it dropped to about 42 per cent. as the steam saturation temperature was raised to 80°. This falling off in quality was partly counter-balanced by an increase in the quantity produced per ton of coal, but the general efficiency fell off as more steam was used. As the steam saturation temperature was raised the gas became richer in hydrogen and carbon dioxide, but much poorer in carbon monoxide; at the same time the net calorific value of the gas fell from 43·6 to 38·69 kilogrammes C. per cubic foot.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1907, No. 1, p. 126.



(b) *Thermal Efficiency of the Plant.*—On raising the steam saturation temperature from  $60^{\circ}$  to  $80^{\circ}$ , using live steam for the blast, the efficiency of the plant fell from 68.7 to 57.8 per cent.

(c) *Yield of Ammonia.*—As far as ammonia recovery was concerned, for high yields the plant should be run with the highest steam saturation temperature consistent with the production of combustible gas.

The ammonium sulphate equivalent of the ammonia in the gas was found to increase from 39 to 72 lbs. per ton of coal gasified as the steam saturation temperature of the blast was raised from  $66^{\circ}$  to  $80^{\circ}$ .

At a saturation temperature of  $60^{\circ}$ , 27 per cent. of the nitrogen in the coal was recovered as ammonia; at a temperature of  $65^{\circ}$ , 30 per cent., and at  $80^{\circ}$ , 50 per cent., was recovered.

The gas-producer first assumed importance in 1856, on the introduction of the Siemens regenerative system. In 1861 the well-known Siemens gas-producer was patented, and is illustrated by fig. 141. It consisted of a chamber lined with fire-brick, with one side sloping at an angle of  $45^{\circ}$  to  $60^{\circ}$ , with the grate at the bottom. The grate thus resembled the step-grate largely used on the Continent. The fuel was charged in at the top of the incline, and fell in a thick bed upon the grate, where air was admitted. Passing from the top of a brick shaft or up-take, 8 to 10 feet high, placed above the producer at the back, there was a cooling tube, having not less than 60 square feet of surface per producer. Its object was to cool the gases issuing from the producer, thus giving them increased density, causing an onward movement towards the furnace, and rendering it unnecessary to place the producer at a much lower level than that of the furnace. This cooling, however, resulted in a condensation of tar, and, to overcome this annoyance, modifications were adopted in the producer and its working. In one modification of Siemens producer the volatile products of distillation are obliged to descend through highly heated fuel, thus causing the tar to undergo decomposition.

The modern Siemens producer is one of the best-known types of grate producers.

This producer is illustrated in fig. 142, and it will be seen that the chief differences between this and the early form consist of the elimination of the cooling tube, the closing of the grate portion, and the alteration in the slope of the front wall and grate.

In fig. 142, D is the hopper by which the fuel is introduced into the rectangular chamber C, F are the firebars, and E the gas-flue through which the gases pass on their way to the furnace. Air is injected by means of the steam jet A, through two openings on each side shown at B.

The ashpit is cooled by water in an iron tray, the water being kept at practically a constant level. The ashes and

clinkers which accumulate on the grate are removed at regular intervals.

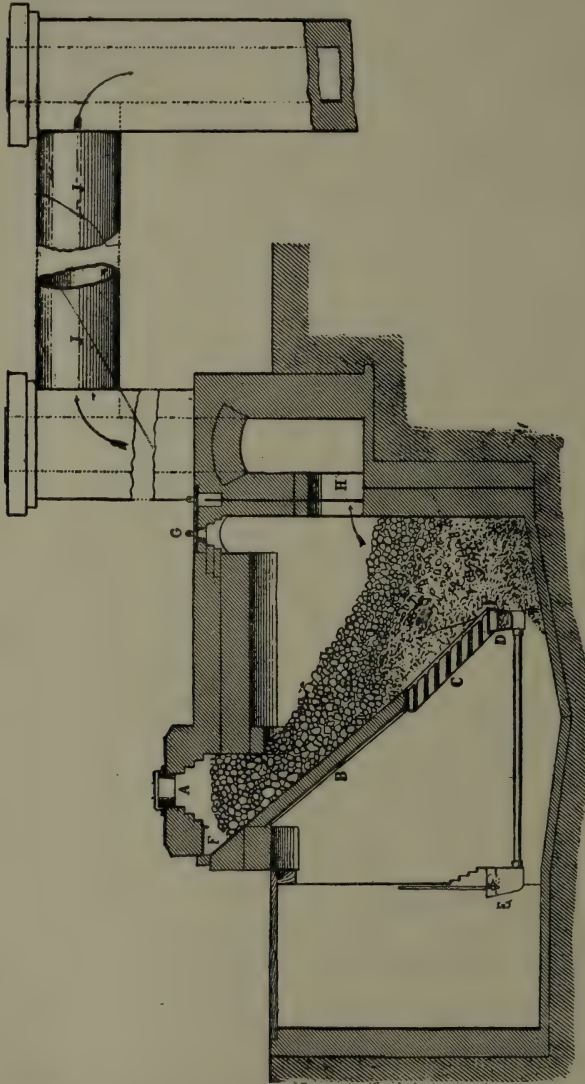


FIG. 141.— Siemens Producer, 1862.

The Wilson gas-producer (fig. 143) represents a type of solid bottom producers, the fuel resting on the bottom, the air and steam being injected through a central passage called the dis-

tributor, supported by a fire-brick arch. The producers are cylindrical, and consist of an outside shell of boiler plate, lined with fire-brick. They vary from 8 to 12 feet in diameter, and gasify about 30 lbs. of coal per square foot of bottom area per hour. The fuel is charged through a central hopper CH, and the gas is drawn off through a series of openings *aaa*, arranged symmetrically round the circumference of the producer to the downcomer B. To remove the ashes in this form of Wilson, the producer has to be stopped at regular intervals, and iron bars are pushed through small openings and allowed to rest on the central

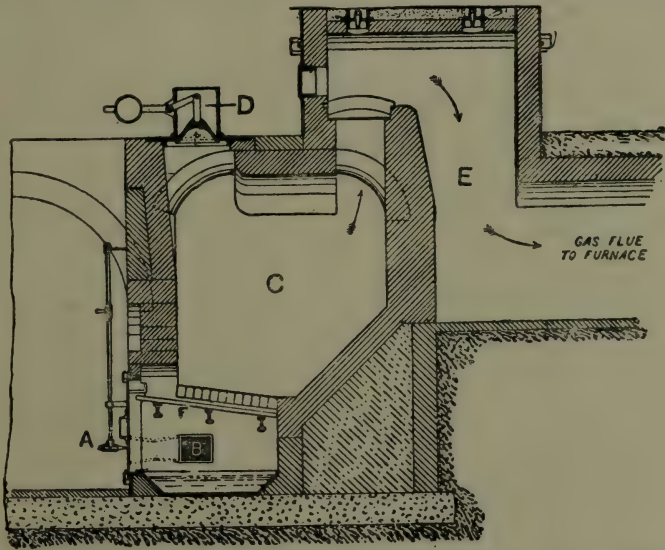


FIG. 142.—Modern Siemens Producer. A, steam injector; B opening through which steam injected; C, body of producer; D, charging hopper; E, gas flue; F, firebars.

fire-brick arch in order to support the fuel. The cleaning doors C are opened and the ashes raked out.

After closing the doors, the temporary firebars are withdrawn, the charge allowed to sink, and the blast turned on.

To avoid this necessary stoppage, later forms are used with a water-sealed bottom, from which the ashes and clinkers can be removed without interfering with the working of the producer, and in one type an Archimedean screw is used, which rotates under the water, and thus removes the ashes.

The Mond producer is one of the latest developments of the gas producer, and was specially designed for the collection and recovery of as large an amount of ammonia as possible as a by-



product. In this form very large quantities of steam are used, about 2 tons for every ton of coal gasified, thus preventing the temperature from rising to such a degree as to bring about the formation of much clinker in the ash, or to decompose the ammonia products from the coal. The greater portion of this steam passes out of the producer undecomposed, but during its condensation its sensible and latent heat are utilised to produce fresh steam for use in the producer. The fuel is mechanically fed into the producers, and is charged in large quantities of 8 to

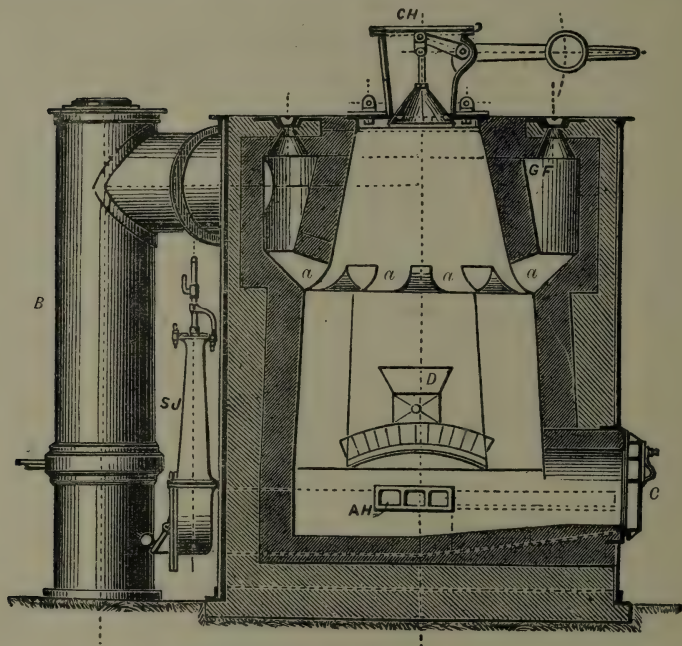


FIG. 143.—The Wilson Producer. *aaa*, openings round circumference of producer through which gas is withdrawn; *B*, downcomer or gas-flue; *C*, door for raking out ashes; *D*, air distributor.

10 cwts. at a time, and the ashes are withdrawn without interfering with the working of the plant. The gas generated is uniform in quality, and on leaving the producer is cooled by passing through the superheaters, round which the air and steam forming the blast travel and become heated.

From the superheaters the gas passes through washers, and thence passes to gas-cooling towers. An exchange of heat between the hot gas and cold water cooling towers is thus effected, and the hot water, leaving the bottom of the tower, is pumped up to the top of an air-heating tower, down which it is allowed



to fall. During its descent it meets the ascending air-blast forced in at the bottom by the blower, whereby another heat exchange is effected and the blast is both heated and charged with steam.

Fig. 144 is a sketch of the producer, which consists of an inner and outer wrought-iron cylindrical shell, the former lined with fire-brick for a portion of its height. The top is arched and is lined with fire-brick, while the bottom portion consists of an inverted truncated cone. The whole producer is supported by cast-iron brackets, and a water-bosh at the bottom forms a seal. The fuel is delivered direct from the railway waggons into a large hopper over the producers, and is charged into the hoppers of the different producers by a creeper. When the hopper is filled, the hood valve is opened, and the fuel falls into the bell-shaped casting suspended from the top of the inside of the producer. This internal bell being surrounded by the hot producer gas, the coal undergoes partial distillation, and the products of distillation having necessarily to pass downwards through some of the hot fuel before they can escape, a portion of the tarry matter is destroyed and converted into gas. At the bottom of the

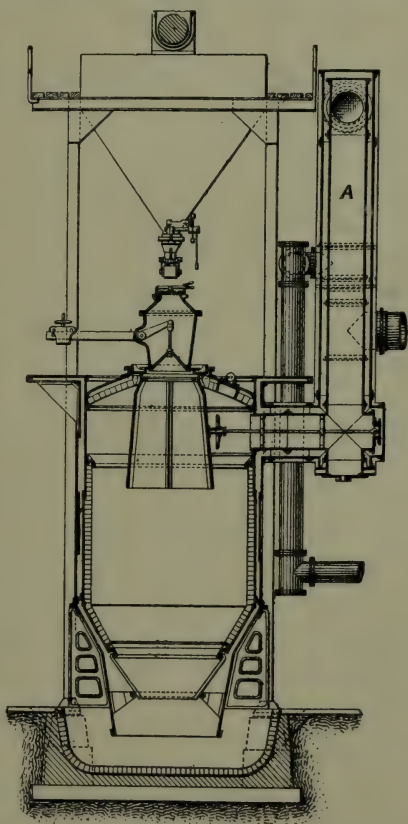


FIG. 144.

producer are two cast-iron rings on which sloping bars are fixed, but as these do not reach the centre, part of the weight of the superincumbent fuel rests upon the ashes, which form a reversed cone, filling the centre space down into the water.

The air and steam forming the blast having passed round the superheater A, pass between the outer and inner iron casings of the producer, and thence to the fire-bars.

It must be remembered that the method of working a Mond producer may vary under varying conditions, and that ammonia recovery can only be profitably undertaken on large plants using about 150 tons of fuel per week. Moreover, the excessive use of steam under such conditions involves the production of a gas rich in carbon dioxide and hydrogen, but poor in carbon monoxide, and, for furnace purposes generally, this is not so efficient a gas as one richer in carbon monoxide, and poorer in carbon dioxide and hydrogen.

The composition of producer gas varies with the fuel used, form of producer, amount of steam, etc., the following table giving the composition of gas produced from various fuels:—

Fuel used.	Nitrogen.	Carbonic Oxide.	Carbonic Anhydride.	Hydrogen.
Wood . . .	53·2 to 55·5	21·2 to 34·5	11·6 to 22·0	0·7 to 1·8
Charcoal . . .	64·9	34·1	0·8	0·2
Peat . . .	63·1	22·4	14·0	0·5
Coke . . .	64·8	33·8	1·3	0·1

The following table gives typical analyses from the producers considered in this chapter:—

	Siemens.	Wilson.	Mond.
Carbonic oxide . . . .	24·8	23·4	11·0
Marsh gas . . . .	2·3	2·9	2·0
Olefiant gas . . . .	...	0·4	...
Hydrogen . . . .	8·7	12·0	29·0
Carbonic anhydride . . .	4·8	5·1	16·0
Nitrogen . . . .	59·6	56·2	42·0
Percentage of combustible gas .	35·8	38·7	42·0

**Water-gas.**<sup>1</sup>—As has already been shown, when steam is decomposed by incandescent carbon, a mixture of hydrogen and carbon monoxide is obtained. This mixture is called water-gas, and has many valuable applications in metallurgical practice.

The reaction is endothermic; and unless heat is supplied from an outside source, the incandescent carbon is rapidly cooled and the reaction ceases. In practice, the gas is made in the following

<sup>1</sup> See *Mineral Industry* for 1900, vol. ix. p. 148.

manner:—An iron cylinder is lined with fire-brick and provided with the necessary apparatus for introducing the coke. When this has been lighted, a current of air is forced in until the mass is brought to a high temperature. The blast is then stopped, the charging aperture is closed, and a jet of steam is passed through the incandescent carbon. The steam is decomposed; its oxygen burns the carbon into carbonic oxide, setting free the hydrogen. The resulting mixture has equal vols. of hydrogen and of carbonic oxide, the weights being as 2 to 28.

There are two distinct modes of procedure for heating up the carbon; in the first, air is blown through as in ordinary gas producer practice, the producer gas thus formed being utilised; the second method is to blow air through under greater pressure, in which case the fuel is completely burnt to carbon dioxide, and about three times the heat developed as in the previous case, whereby the mass of carbon is brought to the incandescent state in a much shorter time. Thus, instead of converting part of the fuel into producer gas, and utilising the heat units contained in this by burning it in another furnace, the whole of the heat units developed from complete combustion of carbon to carbonic dioxide are developed *in situ* in the producer itself, and are thus available for the dissociation of a greater quantity of water and production of a larger quantity of water-gas from a given unit of fuel. This method, devised by Dellwik and Fleischer, has the additional advantage that only one combustible gas is made; as the products of combustion from injecting air, being carbon dioxide and nitrogen, are of no value, they are consequently allowed to escape directly into the air, and the plant is not complicated by having a gas-holder to receive the combustible producer gas produced during the first operation, as in the ordinary process.

Fig. 145 illustrates the latest form of the Dellwik-Fleischer Producer, in which A is the generator, fitted with fire-bars near the bottom, and lined with fire-brick, B is the blast-pipe which admits the air-blast below the fire-grate, C and C' are gas outlets, the upper one, C, being in use when the steam is admitted at the bottom, and the lower one, C', not seen in the sketch, being in use when the steam is admitted at the top; D is the stack for the outlet of waste gases during the heating up with air, this also shows the charging arrangement; E represents the interlocking valve gearing used for reversing the direction of the steam and the water-gas at intervals; F is the steam superheater, from which two conducting pipes enter the generator, one near C and the other near C'; G is the scrubber, through which the water-gas passes on its way to the gas-holder H; I is the blower and engine. In use, the steam is alternately blown in at the top and bottom, the water-gas being drawn off at the bottom or top as the case may be.

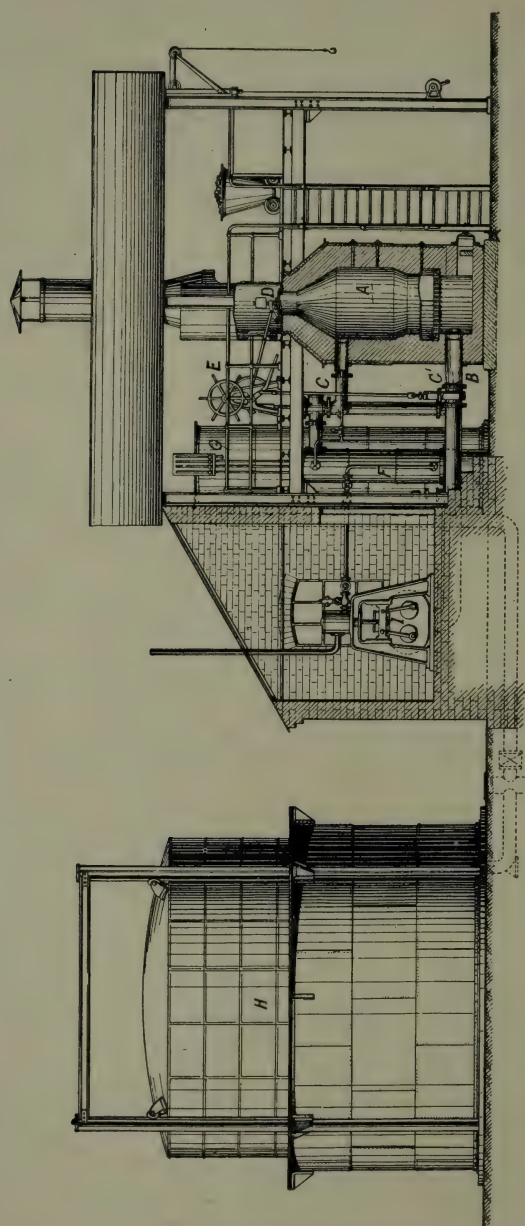


FIG. 145.—The Dellwik-Fleischer Water-Gas Plant. A, generator; B, blast inlet; C, C', gas outlets (the lower, C', behind the blast pipe); D, stack and charging valve; E, interlocking valve gearing; F, steam superheater; G, scrubber; H, gas-holder; I, blower and engine.



Water-gas has approximately the following composition :—

CO	.	.	.	.	.	39.6
H	.	.	.	.	.	50.8
CH <sub>4</sub>	.	.	.	.	.	0.9
CO <sub>2</sub>	.	.	.	.	.	4.7
O	.	.	.	.	.	0.2
N	.	.	.	.	.	3.8

**Blast-furnace Gases.**—In 1814 Aubertot first used the waste gases of blast furnaces for roasting ore, burning lime, and similar purposes, and these gases are now largely used when a very high and uniform temperature is not required. The chief uses are for heating the hot-blast stoves (which are used in turn for pre-heating the blast for the furnaces) for raising steam, and for calcining and roasting ores. The composition of the waste gases varies with the fuel used in the blast furnace, and the following table gives typical examples :—

	N.	CO.	CO <sub>2</sub> .	CH <sub>4</sub> .	H.	C <sub>2</sub> H <sub>4</sub> .
Charcoal . .	59.7-63.4	20.2-29.6	5.9-19.4	0.3-1.0	0.1-0.4	...
Coke . .	64.4	34.6	0.9	...	0.1	...
Coal . .	56.3	21.5	15.2	4.2	1.0	1.8

It will be noticed that these gases are very similar to poor producer gas, the chief difference being the much smaller percentage of hydrogen. Great strides have been made in recent years in the use of these waste gases in gas engines.<sup>1</sup> The chief difficulty<sup>2</sup> formerly met with was the removal of the dust present, but several successful devices have now been designed, and there is no doubt that a great future lies before the use of the immense quantities of these waste gases annually produced for the direct production of power in gas engines. As the mechanical difficulties with large gas engines have been gradually overcome the size of these has been increased. At many works engines of from 700 to 1000 horse-power are now installed for operating the blowing engines, and where steelworks have a large blast-furnace plant attached the gas produced is more than is required for this purpose; the surplus is used for gas engines to generate electricity at a central station, for use in various ways in connection with the steel plant, in some cases the rolling mills being electrically driven.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1899, No. 1, p. 130; 1900, No. 1, p. 109; 1901, No. 2, p. 149; 1906, No. 3, pp. 16, 36, 141.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1905, No. 1, p. 321.

## CHAPTER VIII.

### MATERIALS AND PRODUCTS OF METALLURGICAL PROCESSES.

**Ores.**—This term is applied by the metallurgist only to those minerals from which, on a large scale, metals may be obtained with profit. The ores must be supplied to the works in a suitable condition for smelting, the preliminary washing and dressing operations being carried out at the mine. *Gangue*, vein-stuff, or matrix is the extraneous earthy matter associated with the ore.

Ores contain the metals—(1) in the native or metallic state (examples—gold, silver, copper, mercury); (2) in combination with oxygen as oxides (for example, hæmatite,  $\text{Fe}_2\text{O}_3$ ); (3) as oxides in combination with water (limonite,  $\text{Fe}_2\text{H}_2\text{O}_4$ ); (4) in combination with halogens (horn silver,  $\text{AgCl}$ ); (5) in combination with sulphur, arsenic, and antimony (galena,  $\text{PbS}$ ); (6) in combination with acids as salts (anglesite,  $\text{PbSO}_4$ ); ores also occur in nature in a state of mixture; (7) as various combinations of the same metal (for example, azurite,  $2\text{CuCO}_3 + \text{Cu}(\text{HO})_2$ ); (8) as various combinations of more than one metal in one mineral species (for example, pyrargyrite,  $3\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$ ); lastly, (9) as several mineral species occurring together in the ore deposit, galena and blende, spathic iron ore and iron pyrites.

The value of an ore depends upon the nature of the metal it contains and the difficulty with which its extraction is attended. Thus, iron ores containing less than 25 per cent. of metal are rarely smelted. Ores of iron are not considered rich unless they contain 50 per cent. of metal. Copper ores are rich when they contain 15 per cent. of metal, whilst ores yielding a few ounces of gold per ton are extremely valuable. These relations, however, continually change as new methods of concentration or treatment of poor ores are adopted.

**Fluxes.**—In order to separate the extraneous matter usually contained in a furnace charge of ore and reducing agent, certain materials must be added to form slag. These materials are known as fluxes.

In the smelting processes, earthy, alkaline, and metallic substances are used as fluxes. The alkaline fluxes are expensive, and are rarely used except in refining processes. The following are the principal earthy fluxes in use:—

1. Lime, which acts as a powerful base for removing silica. Lime is used in a pure state or as carbonate. As a rule, limestone is used, especially if the furnace is large. Limestone is largely used in iron smelting, as most iron ores contain an excess of silica. Dolomite, the carbonate of lime and magnesia, is specially useful, but more expensive.

2. Fluorspar (calcium fluoride), which is a useful flux for ores containing silica, barytes, or gypsum. With the two latter it easily fuses. It is also used in the open-hearth furnace to increase the fluidity of the slags and for the removal of sulphur, but on account of its expense its employment is limited. The greater portion of the fluorspar is found unchanged in the slag; it facilitates the fusion, and increases the fluidity of the mass.

3. Barytes, which acts as a powerful base. It is a good sulphurising agent; for example, in the concentration of nickel speise, the copper present with the speise being removed and a regulus formed.

4. Alumina-bearing rocks, such as clay-slate, are used in smelting ores very rich in lime. As a rule, however, the charge is so mixed that argillaceous and calcareous ores are present in suitable proportions.

5. Siliceous materials, such as quartz, natural silicates, siliceous slags, are used when the ores contain an excess of basic materials that have to be removed.

6. Oxides and carbonates of iron, basic iron slags, etc., are used in the smelting of siliceous ores, especially of lead and copper, and also in the recovery of valuable metals from slags, residues, and waste.

**Metallurgical Agents.**—The metallurgical agents chiefly used are—1. Metals, either for decomposing the combinations of other metals, or as a means of concentration. Thus iron is used for decomposing galena, zinc for desilverising argentiferous lead, and mercury for concentrating gold.

2. Metallic oxides are used for purifying the raw metal in refining processes. Thus iron ore or hammer-scale is used for refining iron, and as a flux in lead and copper smelting.

3. Slags serve to increase the fluidity of the furnace charge, or mixtures of slags may be used for recovering the metals they contain, and lastly for preventing “scaffolding” or choking of the furnace when pulverised ores are smelted. Their chemical action varies with their composition; basic slags are able to take up a large proportion of silica, while acid slags readily absorb bases. Alkaline slags are rarely used except in crucible processes, as in assaying.



4. Iron pyrites ( $\text{FeS}_2$ ) and magnetic pyrites ( $\text{Fe}_7\text{S}_8$ ) exert a reducing action on oxides by giving up sulphur and forming sulphurous anhydride. Certain sulphides, such as zinc sulphides, infusible alone, may be rendered fusible by the addition of iron pyrites.

In the roasting of ores in furnaces or in piles the following chemicals are used:—(1) Salt, for the formation of silver chloride in the treatment of silver ores; (2) Lime, for the absorption or separation of the acids formed on roasting copper regulus, etc.; (3) Ferrous sulphate, in the treatment of silver ores containing a little iron pyrites.

**Selection of Fluxes.**—In the choice of fluxes, when the gangue is siliceous, at least two bases must be added in order to form a fusible silicate. When the gangue is argillaceous, a single base is sufficient to form a double silicate. When the gangue is basic, that is, containing lime, magnesia, alumina, or iron, a siliceous flux must be added. Quartz alone is sufficient if the gangue already contains two or more bases, but if there is but one base, clay or some other silicate must be added with the quartz. Siliceous slags may be advantageously used for the purpose.

**Slags.**—The silicates formed in metallurgical processes by the combination of silica with the earths and metallic oxides are termed *slags*. As a rule, slags are smelters' refuse. In the refining of metals, however, slags are frequently formed by the oxidation of the metallic impurities. Such slags consist largely of metallic oxides, and are smelted again in order to recover the large proportion of metals they contain. These slags may be distinguished as cinder or scoria.

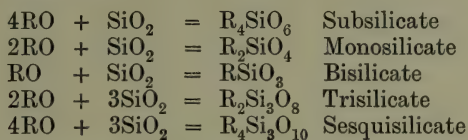
The bases that occur in silicate slags, mostly combined with the silica, are—lime, alumina, magnesia, rarely ferric and manganic oxides, ferrous oxide, manganous oxide, zinc oxide, more rarely baryta, and alkalis in slags of all blast furnaces using charcoal as fuel, and, in addition to these, small amounts of the metals that are being smelted are invariably present, partly in chemical combination with the silica, and partly in other combinations mechanically mixed with the slag.

Some oxides and earths, such as zinc oxide and alumina, not only interfere with the fluidity of the slag, but also cause a scum to form which is difficult to separate from the slag. In many slags, calcium fluoride is found. The calcium fluoride melts without decomposition, and is merely in a state of mechanical mixture with the slag. This is also the case with the calcium sulphide frequently met with in blast-furnace slags.

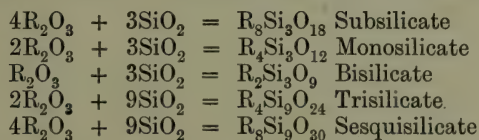
Silica consists of one atom of silicon and two atoms of oxygen, so that the various silicates have the compositions given below.  $2\text{RO} + \text{SiO}_2$  is the monosilicate or neutral silicate of the metallurgist. It contains in acid and base equal amounts of oxygen, whilst the neutral silicate of the chemist, which has the formula



$\text{RO} + \text{SiO}_2$ , is termed a bisilicate by the metallurgist, because the acid contains twice as much oxygen as the base. The series of formulæ for silicates is—



For bases having the composition  $\text{R}_2\text{O}_3$  the formulæ are—



The quantities of oxygen in the bases bear the following proportions to those in the acids in the various silicates:—

	O in base :	O in acid.
Subsilicate . . . . .	2 :	1
Monosilicate . . . . .	1 :	1
Bisilicate . . . . .	1 :	2
Trisilicate . . . . .	1 :	3
Sesquisilicate . . . . .	2 :	3

Every sesquisilicate may be resolved into a monosilicate and a bisilicate: thus  $\text{R}_4\text{Si}_3\text{O}_{10}$  is equal to  $\text{R}_2\text{SiO}_4 + 2(\text{RSiO}_3)$ , and  $\text{R}_8\text{Si}_9\text{O}_{30}$  is equal to  $\text{R}_4\text{Si}_3\text{O}_{12} + 2(\text{R}_2\text{Si}_3\text{O}_9)$ . If a silicate contains but one base it is termed a monobasic or simple silicate, but if two or more bases are present it is termed a double silicate or a multibasic silicate, and in the formula the silicates of the various bases are united by a plus sign.

A classification of the silicates as ortho- and meta-silicates, based upon their analogies to phosphates, was suggested by Odling,<sup>1</sup> but it has not come into use amongst metallurgists.

The fusibility of slags is dependent on the amounts of silica and bases they contain. As a rule, the subsilicates are very fusible, forming a limpid liquid; they consolidate very rapidly, and split up in so doing. They have usually a dark colour and, on account of the large proportion of bases they contain, a high specific gravity. The monosilicates are less fusible, and do not form so limpid a liquid. The bisilicates are less fusible still; they form a viscous mass, which may be drawn out into threads. They are usually glassy and consolidate slowly. The trisilicates also flow very slowly, consolidate slowly, and require a very high temperature for their formation.

The most fusible silicates are those of the alkalies, next those

<sup>1</sup> *Phil. Mag.*, vol. xviii. (1859), p. 368.

of lead, iron, manganese, and copper, and last the earthy silicates. The most desirable silicate depends upon the nature of the operation. Blast-furnace slags from iron smelting are mostly monosilicates or bisilicates. Those in lead smelting are generally monosilicates,<sup>1</sup> although a sesquisilicate is, under certain conditions, desirable.

**Economic Application of Slags.**—The slags obtained in smelting metals other than iron are largely used as fluxes in various metallurgical processes for taking up either the silica or the bases, or, when they are ferruginous, for precipitating purposes. Occasionally the slags are moulded into bricks, and used for walls or other light constructions.

The slags obtained in iron smelting are used, if not too glassy, for macadamising roads. For the ballast of railway lines glassy slags may advantageously be used, as the mass is very permeable and keeps the sleepers dry. In the form of large blocks, they may be used for road-making. They may be moulded into bricks, the best results being obtained when the moulded bricks are kept at a white heat for several hours in a tightly closed space, whereby they are devitrified, and become considerably harder if they are allowed to cool slowly under a cover of coal dust and ashes. Good bricks may be made of granulated slag mixed with lime, the proportions being usually 10 parts of slag sand to 1 part of lime. Blast-furnace slag, if not too acid, may be burnt in a state of powder with lime, and gives an hydraulic cement almost equal to Portland cement.<sup>2</sup>

The manufacture of slag cement has of recent years acquired so considerable a development that it may safely be said that an advantageous method of utilising blast-furnace slag has at length been found. The following are analyses of slags actually used for this purpose :—

	Middles- brough.	Bilbao, Spain.	Saulines, France.	Choindez, Switzer- land.	Harz- burg, Germany.	Belgium.
Lime . . . .	32·75	47·30	47·20	45·11	48·59	44·75
Silica . . . .	30·00	32·90	31·65	26·88	35·72	32·51
Alumina . . . .	28·00	13·25	17·00	24·12	16·40	13·91
Ferrous oxide . . . .	0·75	0·46	0·65	0·44	0·43	0·48
Magnesia . . . .	5·25	1·37	1·36	1·09	1·28	2·20
Calcium sulphide . . . .	1·90	3·42	...	1·86	2·16	4·90
Manganese oxide . . . .	0·60	1·13	0·85	0·50	traces	0·60
Residue . . . .	0·75	0·17	1·29	...	0·42	0·65
Totals . . . .	100·00	100·00	100·00	100·00	100·00	100·00

<sup>1</sup> Collins, *Metallurgy of Lead*, p. 113.

<sup>2</sup> *Inst. Mech. Eng.*, 1892, p. 70; *Stahl und Eisen*, xxiii. pp. 361–375.

The slag is run into water so as to render it easy to obtain slag sand. This is ground under edge-runners, and the pasty mass is spread on drying plates. The dried slag is then ground under millstones to a fine powder and sifted to exclude coarse particles. Freshly burnt lime is slaked, and then carefully screened, and 25 per cent. of this slaked lime is thoroughly mixed with 75 per cent. of slag sand.

The specific gravity of this cement is very low as compared with Portland cement, whilst the time occupied in setting is comparatively long. For purposes of storage it compares well with Portland cement. By exposure to the air it absorbs carbonic anhydride more rapidly than does Portland cement, but it does not deteriorate greatly by long exposure. Owing to the closeness of the particles, this cement appears to be well adapted for works under water, such as docks or breakwaters.

Blast-furnace slag is also largely used for the production of slag wool or silicate cotton, which is obtained by causing steam to impinge on to a jet of molten slag in such a way that the steam jet encounters only a half of the slag jet. Slag wool is extremely light and fireproof. It is a good non-conductor of heat and of sound, and it is so porous that it will absorb large quantities of water. It is used for covering steam and hot-air pipes. In Silesia and other localities, where ironworks and collieries are in close proximity, blast-furnace slag is largely used for filling the excavations from which the coal has been removed. Finely pulverised blast-furnace slag has been found in Sweden to be an excellent manure for moor land which is deficient in lime, as well as for clay and sandy soils.

The slag obtained in the basic Bessemer process, on account of its high percentage of phosphorus, forms a valuable manure. Many thousands of tons of slag are annually employed for this purpose, it having been found that the phosphorus it contains is in a form that is very readily assimilated by the plants. The utilisation of basic Bessemer slag is referred to in a subsequent chapter.<sup>1</sup>

**Calculation of Furnace Charges.**—In order to obtain the greatest possible yield of metal with the least consumption of fuel, care must be taken to have a proper mixture of ore and flux. Ores reducible with difficulty should be mixed with fluxes that render the charge pasty, so that the slag-forming constituents do not melt before the metals are reduced from their combinations. When raw coal or coke is used as fuel, the quantity and composition of the ash must be taken into consideration, as this always contains silica. With charcoal as fuel this may be neglected, as the percentage of ash is always low, and the ash itself, which is strongly alkaline, is a useful flux.

As an example of the calculations necessary, a charge of iron ore

<sup>1</sup> Methods of utilising slag are fully described by G. Redgrave, *Journ. Soc. Arts*, vol. xxxviii. (1890), p. 221.



may be selected which is to be smelted with coke to grey pig-iron, and for which the necessary amount of lime as flux is required to be determined. For the example now to be given the author was indebted to Prof. C. A. M. Balling, Director of the School of Mines at Příbram in Bohemia, who has permitted him to borrow it from his valuable treatise on metallurgical chemistry.<sup>1</sup>

Let it be assumed that there are to be smelted four varieties of ore having the following compositions :—

	Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
A.	54	7	2	...	12	...
B.	47	8	1	1	15	...
C.	38	10	2	1	24	1
D.	40	9	2	1	20	...

In order to simplify the calculations whole numbers are taken, and the percentages of water and carbonic anhydride are disregarded. The ore to be used as flux (I.) and the 10 per cent. of ash (II.) in the coke have the following percentage compositions :—

	Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
I.	25	4	25	4	6	...
II.	12	35	1	1	44	0·5

For the production of 100 parts by weight of iron, 190 parts by weight of coke are necessary.

In view of the large proportion of silica in the ores C and D, high percentages of these ores are inadmissible in the charge. The ore A, on the other hand, is the best, and must therefore form the greater portion of the charge, which is to be mixed so as to contain on an average 45 per cent. of iron. Taking into account the important constituents of the ores, the following weights would be selected for the charge :—

Ore B.	Ore C.	Ore D.	Flux.	Total.
25	10	15	15	65

It must now be calculated how much iron and slag-giving constituents this mixture contains in order to determine the quantity of ore A that must be added to give an average of 45 per cent. of iron. In this way, by proportion, the following amounts of the various constituents are calculated to be present :—

	Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
25 parts of B contain . .	11·75	2·00	0·25	0·25	3·75	...
10 " C " . .	3·80	1·00	0·20	0·10	2·40	0·10
15 " D " . .	6·00	1·35	0·30	0·15	3·00	...
15 " flux " . .	3·75	0·60	3·75	0·60	0·90	...
65 Totals .	25·30	4·95	4·50	1·10	10·05	0·10

<sup>1</sup> *Compendium der metallurgischen Chemie*, Bonn, 1882.



Regarding this ore-mixture as a single ore the percentage composition will be as follows :—

Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
38·92	7·61	6·92	1·69	15·46	0·15

With this ore, or rather mixture containing 38·92 per cent. of iron, it is required to mix the ore A so as to bring the charge to 45 per cent. of iron. If the ore mixture is represented by  $x$  we have the following equation :—

$$\begin{aligned}x + A &= 100 \\ 38·92x + 54A &= 100 \times 45\end{aligned}$$

On solving this equation, A is found to be 40·5, and  $x = 100 - A = 59·5$  parts by weight. The equation thus requires that 40·5 parts of the ore A should be mixed with 59·5 parts of the ore-mixture chosen, and consequently the 65 parts must be reduced by proportion to 59·5, giving the following percentages as the definite composition of the charge :—

Ore A.	Ore B.	Ore C.	Ore D.	Flux.	Total.
40	23	10	13	14	100

In this charge the percentages of the various constituents are found by proportion to be as follows :—

	Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
In 40 parts of A . . .	21·60	2·80	0·80	...	4·80	...
23 „ B . . .	10·80	1·84	0·23	0·23	3·45	...
10 „ C . . .	3·80	1·00	0·20	0·10	2·40	0·10
13 „ D . . .	5·20	1·17	0·26	0·13	2·60	...
14 „ flux . . .	3·50	0·56	3·50	0·56	0·84	...
100 Totals .	44·90	7·37	4·99	1·02	14·09	0·10

For the production of 100 parts of iron,

$$100 : 45 = x : 100.$$

$x = 222·2$  parts of this charge are required, and in this are contained the following weights of iron and slag-giving constituents :—

Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
99·77	16·40	11·09	2·26	31·30	0·22

For its production, 190 parts of coke are required, the ash of which, according to the analysis, contains—

Fe.	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	SiO <sub>2</sub> .	S.
2·28	6·65	0·19	0·19	8·36	0·95

It is therefore necessary to remove as slag:  $\text{Al}_2\text{O}_3$  23·05;  $\text{CaO}$  11·28;  $\text{MgO}$  2·45;  $\text{SiO}_2$  39·66;  $\text{S}$  1·17.

For the formula  $\text{Al}_4\text{Si}_3\text{O}_{12} + \text{Ca}_2\text{SiO}_4 + \text{Mg}_2\text{SiO}_4$ , representing a monosilicate, the amount of silica slagged by the bases may be found by proportion with the aid of the atomic weights, thus:—

$$\begin{aligned} 2\text{Al}_2\text{O}_3 : 3\text{SiO}_2 &= 205\cdot6 : 180 = 23\cdot05 : x ; x = 20\cdot18 \\ 2\text{CaO} : \text{SiO}_2 &= 112 : 60 = 11\cdot28 : y ; y = 6\cdot04 \\ 2\text{MgO} : \text{SiO}_2 &= 80 : 60 = 2\cdot45 : z ; z = 1\cdot83 \end{aligned}$$

—giving a total  $(x + y + z)$  of 28·05 parts by weight of silica, so that  $39\cdot66 - 28\cdot05 = 11\cdot61$  parts of silica remain to be converted into slag. According to the same proportion—

$$\text{SiO}_2 : 2\text{CaO} = 60 : 112 = 11\cdot61 : a.$$

From which  $a$  is found to be 21·7 parts by weight of lime base, which, as calcium carbonate contains but 56 per cent. of  $\text{CaO}$ , is contained in 38·7 parts of calcium carbonate.

Similarly, for removal as calcium sulphide, the sulphate requires, according to the proportion  $\text{S} : \text{CaO} = 32 : 56 = 1\cdot17 : \beta$ ,  $\beta = 2\cdot05$  parts of lime, which amount is contained in 3·65 parts of calcium carbonate. Consequently, altogether there is required  $38\cdot7 + 3\cdot65 = 42\cdot35$  parts of calcium carbonate. But as this is added in the form of impure limestone containing only some 95 per cent. of calcium carbonate, the quantity to be added will be 44·58 parts. As this amount, however, is required for 222 parts of charge, 100 parts will require 20·1 parts of limestone as flux. In this example, the small quantity of limestone required is explained by the fact that 14 parts of fluxing ore, containing 25 per cent. of lime, have already been added.

The following is an example of South Wales practice, prepared for the author by Mr H. Raleigh. Four ores, all of which are siliceous, have been taken, namely:—

	Iron.	Alumina.	Lime.	Magnesia.	Silica.	Sulphur.
A.	57	3	...	...	8	...
B.	49	6	1	1	14	...
C.	48	2	1	2	18	...
D.	47	3	2	...	12	...

And of these A is a “rich” red hematite, B is “soft” red hematite, C a “hard” red hematite, D is “rubio” (S) ore.

For the production of 100 parts by weight of pig-iron, 100 parts by weight of coke are found to be necessary; this coke contains 10 per cent. of ash, and its composition is as follows:—

	Iron.	Alumina.	Lime.	Magnesia.	Silica.	Sulphur.	Carbon and Moisture.
I.	0·2	4·4	0·2	0·1	4·8	1·0	90

A more or less arbitrary mixture of the ore on the principles already explained will be—

Ore A . . .	20 parts	Ore B . . .	20 parts			
Ore C . . .	40 parts	Ore D . . .	20 parts			
		Iron.	Alumina.	Lime.	Magnesia.	Silica.
20 parts of A contain	11·4	0·6	...	...	...	1·6
20 " B "	9·8	1·2	0·2	0·2	...	2·8
40 " C "	19·2	0·8	0·4	0·8	...	7·2
20 " D "	9·4	0·6	0·4	...	...	2·4
Totals	49·8	3·2	1·0	1·0	...	14·0

—and as the total number of weights of ore taken happens to be 100, the total contents are percentages.

The pig-iron produced has a percentage composition—

Iron.	Graphite.	Combined Carbon.	Silicon.	Sulphur.	Phosphorus.
93	3·9	0·22	2·8	0·03	0·05

For the production of 100 parts of pig-iron containing 93 per cent. of iron, 186·7 parts of ore are necessary :—

$$49·8 : 100 :: 93 : x \quad x = 186·7.$$

In 186·7 parts of ore the following weights of iron and slag-giving constituents are contained :—

Iron.	Alumina.	Lime.	Magnesia.	Silica.
93	6·0	1·87	1·87	26·13

For its production, 100 parts of coke are required, containing—

Iron.	Alumina.	Lime.	Magnesia.	Silica.	Sulphur.
0·2	4·4	0·2	0·1	4·8	1·0

The pig-iron contains 2·8 parts of silicon, reduced from 6 parts of silica, so that it is necessary to remove as slag  $30·93 - 6 = 24·93$  silica, 10·4 alumina, 2·07 lime, 1·97 magnesia, and 1·0 sulphur. The slag invariably contains a little iron which may be brought as low as 0·2 per cent. = 0·26 ferrous oxide, and, putting  $p, x, y, z$  as the amount of silica required to flux off the alumina, lime, magnesia, and iron respectively,—

$$\begin{aligned} 2 \text{ Al}_2\text{O}_3 : 3 \text{ SiO}_2 &= 205·6 : 180 = 10·4 : p ; p = 9·1 \\ 2 \text{ CaO} : \text{SiO}_2 &= 112·0 : 60 = 2·07 : x ; x = 1·1 \\ 2 \text{ MgO} : \text{SiO}_2 &= 80·0 : 60 = 1·97 : y ; y = 1·5 \\ 2 \text{ FeO} : \text{SiO}_2 &= 144·0 : 60 = 0·26 : z ; z = 0·1 \end{aligned}$$

$(p + x + y + z) = 11·8$  parts by weight of silica, so  $24·93 - 11·8 = 13·13$  parts of silica, besides 1·0 sulphur, remain to be converted into slag by the addition of limestone, according to the following ratios—

$$\begin{aligned} \text{SiO}_2 : 2 \text{ CaO} &= 60 : 112 = 13·13 : a ; a = 24·5 \text{ parts of lime} \\ \text{S} : \text{CaO} &= 32 : 56 = 1·0 : b ; b = 1·75 \text{ parts of lime} \end{aligned}$$

—and putting  $a, b$ , as the amounts of lime required to satisfy the silica and sulphur respectively, the total lime required will be 26.25 parts, and these are contained in 46.87 parts of calcium carbonate. The limestone used contains 97 parts of calcium carbonate, 1.0 part alumina, and 1.5 part silica. The 1 part of alumina slags off 0.88 part of the silica, leaving 0.62 part silica to consume 2.07 parts of calcium carbonate. The available calcium carbonate then is  $97 - 2.07 = 94.93$  per cent. of the limestone added,

$$\text{and } \frac{100}{94.93} \times 46.87 = 49.37 \text{ parts of limestone.}$$

The slag obtained in the production of 100 parts of pig-iron would be 68.2 parts, made up as follows:—

	Parts.		Per cent.	
Silica	25.67	} = {	Silica	37.6
Alumina	10.90		Alumina	16.0
Magnesia	1.97		Magnesia	2.9
Ferrous oxide	0.26		Ferrous oxide	0.4
Lime	27.15		Lime	39.8
Calcium sulph.	2.25 (1 pt. sulphur)		Calcium sulphide	3.3
	<hr/> 68.20		<hr/> 100.0	

Composition of slag obtained by analysis:—

	Per cent.				Per cent.	
Silica	37.2	}	or expressed thus	}	Silica	37.2
Alumina	15.4				Alumina	15.4
Magnesia	2.3				Ferrous oxide	0.8
Ferrous oxide	0.8				Lime	41.0
Lime	43.3				Magnesia	2.3
Sulphur	1.32				Calcium sulph.	2.97
	<hr/> 100.32				<hr/> 99.67	

All these tedious calculations may be reduced to a few multiplications and additions by employing the accompanying table (p. 305) that has been computed by Prof. Balling.

In order to show the simplicity of the use of this table, the same problem may be solved with its aid. For ascertaining the amount of silica converted into slag by the bases in the charge Table B is used. In the section for monosilicates, the corresponding figures are found for the bases present, and these figures multiplied together give the following products:—

$\text{Al}_2\text{O}_3$	.	.	.	.	23.05	$\times$	0.873	=	20.12
$\text{CaO}$	.	.	.	.	11.28	$\times$	0.535	=	6.04
$\text{MgO}$	.	.	.	.	2.45	$\times$	0.750	=	1.84

Total . = 28.00



Thus 28.00 parts of silica (28.05 in the previous calculation) are converted into slag; and of the total amount, 39.66 parts of silica present, there remain  $39.66 - 28.00 = 11.66$  parts to be converted into slag by the addition of lime. On referring to Table A, it will be seen that the corresponding amount of lime is 1.86, the product being  $11.66 \times 1.86 = 21.69$ . Lastly, for the formation of calcium sulphide, 1 part of sulphur requires  $\frac{56}{32} = 1.75$  of lime, and there is 1.17 part of sulphur to be passed into the slag. This requires  $1.17 \times 1.75 = 2.047$  parts of lime. Thus, altogether  $21.69 + 2.047 = 23.737$  parts of lime are required. One part of lime is contained in  $\frac{100}{56} = 1.785$  of calcium carbonate; the required addition of limestone as flux is therefore  $23.737 \times 1.785 = 42.37$  parts (as compared with 42.35 in the previous solution).

TABLE A. For ascertaining the necessary amounts of Bases to convert given amounts of Silica into slag.		TABLE B. For ascertaining the necessary amounts of Silica to convert given amounts of Bases into slag.	
One part by Weight of Silica requires—	Parts by Weight of Bases.	One part by Weight of Base requires—	Parts by Weight of Silica.
For Monosilicates—		For Monosilicates—	
Lime . . . . .	1.86	Lime . . . . .	0.535
Magnesia . . . . .	1.33	Magnesia . . . . .	0.750
Alumina . . . . .	1.14	Alumina . . . . .	0.873
Ferrous oxide . . . . .	2.40	Ferrous oxide . . . . .	0.416
Manganous oxide . . . . .	2.36	Manganous oxide . . . . .	0.422
For Bisilicates—		For Bisilicates—	
Lime . . . . .	0.93	Lime . . . . .	1.070
Magnesia . . . . .	0.66	Magnesia . . . . .	1.500
Alumina . . . . .	0.57	Alumina . . . . .	1.747
Ferrous oxide . . . . .	1.20	Ferrous oxide . . . . .	0.833
Manganous oxide . . . . .	1.18	Manganous oxide . . . . .	0.845
For Sesquisilicates—		For Sesquisilicates—	
Lime . . . . .	1.24	Lime . . . . .	0.803
Magnesia . . . . .	0.88	Magnesia . . . . .	1.125
Alumina . . . . .	0.76	Alumina . . . . .	1.310
Ferrous oxide . . . . .	1.60	Ferrous oxide . . . . .	0.625
Manganous oxide . . . . .	1.57	Manganous oxide . . . . .	0.633

In order to entirely obviate the necessity for any calculation whatever, Prof. Balling has devised a method of solving the problem graphically. The method is based on the similarity of triangles. From any point *a* (fig. 146) two lines are drawn at right angles, and these form two sides of a right-angled triangle. The co-ordinate lines are divided into equal parts. If as many parts of one line are taken as there are equivalents of acid in the

slag to be formed, and, similarly, as many parts of the other line as there are equivalents of base, and if the end points of the two sides of the triangle are joined by the hypotenuse, then it is merely necessary to draw from any given point in one side a line parallel to the hypotenuse in order to find on the two sides the equivalent amounts of base and acid in the given silicate.

Fig. 146 is a reduced sketch of the triangles for the monosilicates of the earths that are usually required. For practical purposes the best unit of length to adopt is the centimetre, so that tenths (millimetres) and half-tenths may be read. As, however,

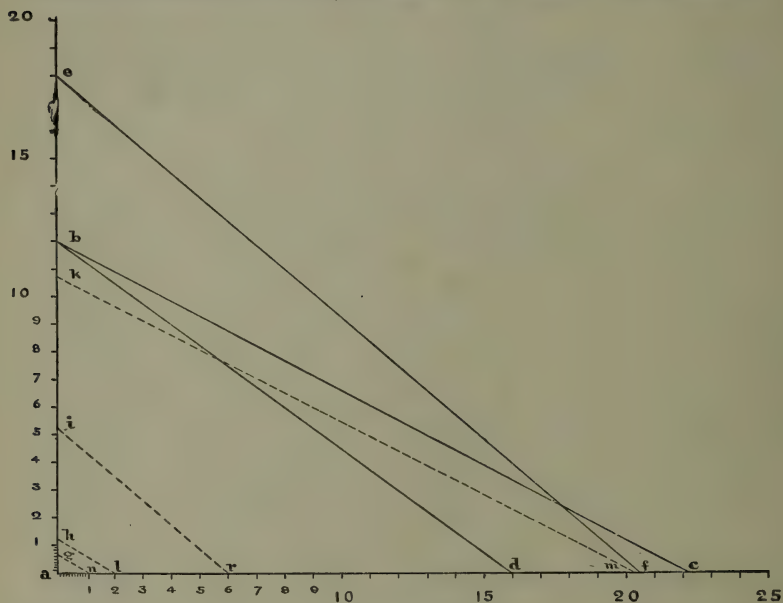


FIG. 146.

the triangles on this scale would be too large, and as only lower figures are used, the triangles may be drawn on a reduced scale, for which the following scheme will be found to answer under all conditions:—

The lime monosilicate requires for base  $2\text{CaO} = 2 \times 56 = 112$  units of length, and for perpendicular  $1\text{SiO}_2 = 60$ . The magnesia monosilicate requires for base  $2\text{MgO} = 2 \times 40 = 80$ , and for perpendicular  $1\text{SiO}_2 = 60$ . Lastly, the alumina monosilicate requires for base  $2\text{Al}_2\text{O}_3 = 2 \times 102.8 = 205.6$ , and for perpendicular  $3\text{SiO}_2 = 3 \times 60 = 180$ . These lengths are reduced in the triangles for monosilicates of lime and magnesia by one-fifth, and in the triangle for the monosilicate of alumina by one-tenth. Thus

the triangle  $abc$  is that of the lime silicate,  $ab$  containing  $\frac{60}{5} = 12$  units of length for silica, and  $ac \frac{112}{5} = 22.4$  units for lime. Similarly, in the triangle  $abd$  representing the magnesia silicate,  $ab$  contains 12 units for silica, and  $ad \frac{80}{5} = 16$  units for magnesia. Lastly, in the triangle  $ae f$ , representing the alumina silicate,  $ae$  contains  $\frac{180}{10} = 18$  units for silica, and  $af \frac{205.6}{10} = 20.56$  units for alumina.

As an illustration of the application of the graphic method, let it be assumed that in a coke blast furnace a charge has to be smelted in which the constituents to be converted into slag average

CaO.	MgO.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .
2	1	6	18

The amount of lime to be added is determined in the following manner:—In order to determine the amount of silica converted into slag by the bases already present, from the point  $l$ , representing the units of base (in this case 2 parts), a line is drawn parallel to the hypotenuse of  $bc$  of the lime triangle. This cuts the perpendicular, representing the silica units, at the point  $h$ , and the length  $ah$  represents the units of weight of silica which slag off the lime already present in the charge. Similarly, the line  $gn$  drawn parallel to  $bd$  shows the amount of silica required by 1 part of magnesia, and the line  $ir$ , drawn parallel to  $ef$ , that required by 6 parts of alumina. On measuring these lengths with the dividers on a decimal scale they are found to be:  $ah = 1.07$ ;  $ag = 0.75$ ;  $ai = 5.23$ ; giving a total of 7.05 units as the amount of silica slagged by the bases present in the charge, and there consequently remains  $18 - 7.05 = 10.95$  parts of silica to be converted into slag by the addition of lime. If, then, from the point  $k = 10.95$  parts of silica, a line is drawn parallel to the hypotenuse of the lime silicate, it cuts the base line at the point  $m$ , which represents 20.15 parts of lime, an amount contained in  $20.36 \times 1.785 = 36.34$  parts of calcium carbonate.

This method is extremely rapid, and, with careful graduation, gives results of great accuracy. In order to apply the method to bisilicates, the amount of silica must be doubled, or those of the bases must be halved.

A purely mechanical method possesses certain advantages, and Prof. Balling's table has been simplified by Mr H. C. Jenkins, who devised a special slide rule for the use of the students of the Royal School of Mines, by the aid of which the calculations can be made with great facility (fig. 147). It consists of two equal scales at right angles, one of which ( $a$ ) is fixed to

a small board, whilst the other (*b*) is fixed at right angles to *a* upon a block (*c*), which is capable of sliding motion in a groove.<sup>1</sup>

The point A, given by the intersection of the zeros of the two scales, is marked upon the board, and from it a line A B parallel to the groove is drawn. With A as centre, lines A C, A D, A E are also drawn, making with A B angles whose tangents are equal to the ratios between the weight of silica to weight of base in the respective silicates which it is desirable to produce in order to

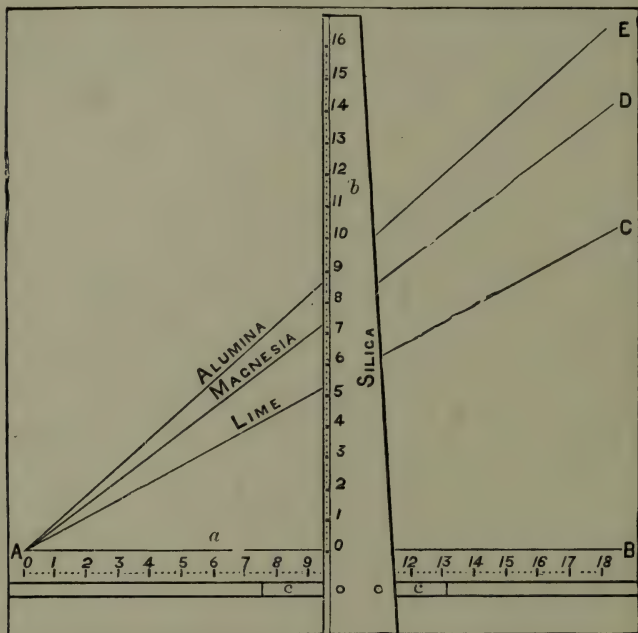


FIG. 147.

form the typical fusible slags ordinarily met with in blast-furnace practice. The lines A C, A D, A E are marked with the names of the bases for which they have been calculated. Thus A C makes an angle of  $28^{\circ} 10'$  with A B, this angle having a tangent whose value is 0.5357, which is the ratio of the molecular weight of silica to twice the molecular weight of lime, and corresponds to calcium silicate; this line therefore is marked "Lime."

Similarly the line A D makes an angle of  $36^{\circ} 52'$  with A B, the value of whose tangents is 0.75, or the ratio of the molecular weight

<sup>1</sup> *Journ. Iron and Steel Inst.*, pt. i., 1891, p. 151.



of  $\text{SiO}_2$  to the molecular weight of  $2\text{MgO}$ ; hence it is marked "Magnesia."

Also the line A E is at an angle of  $41^\circ 25'$ , and this, having a tangent corresponding to the ratio of the molecular weight of  $3\text{SiO}_2$  to that of  $2\text{Al}_2\text{O}_3$ , makes the line correspond to the values of the component parts of silica and of alumina in aluminium silicate, and so it is marked "Alumina."

With such a scale it is a very simple matter to at once read off either the excess of silica in any ore, or the amount required to properly flux off the earthy bases present.

As an example, take an ore containing—

		Silica required.
FeO	. . . 50	...
MgO	. . . 3	2.25
CaO	. . . 5	2.68
$\text{Al}_2\text{O}_3$	. . . 3	2.65
$\text{SiO}_2$	. . . 3	...
$\text{CO}_2$	. . . 36	...

Then, setting the movable scale  $b$  against 3 on the fixed scale  $a$ , and looking along  $b$  until the line marked "Magnesia" cuts it, the value 2.25 is found as being the amount of silica required to satisfy the magnesia. In like manner, the amount (2.68) of silica required for the lime is found, and the amount (2.65) for the alumina respectively; adding all these together, the total of 7.58 parts of silica required for every hundred of the ore is obtained. But there are already three parts present, so every hundred parts of the ore require  $7.58 - 3 = 4.58$  parts of silica to flux it. The gangue of the ore is basic to that extent, and the ore itself can be ticketed in the works as—

C. 607.

Fe. 38.8 per cent.

Basic gangue, needing 4.58 per cent.  $\text{SiO}_2$ .

Another parcel of ore might be found to be deficient in bases, and to require, say, bases to neutralise four parts of silica to every hundred parts of ore. If it contained 35 per cent. iron, its label might be—

E. 1000.

Fe. 35 per cent.

Acid gangue, yielding 4 per cent.  $\text{SiO}_2$ .

If there is any considerable proportion of ash from the coke, as is often the case, it can be entered as acid or basic, just as in the case of an ore, thus :—

Acid, yielding 2 per cent. silica,

or

Basic, requiring 1 per cent. silica,

and the amount of silica for each part of iron present added (or deducted, as the case may be) to each ore in proportion to the number of parts of iron contained in it.

Any small quantity of sulphur can be considered to be one-half its own amount of silica, or a special vertical scale employed, the length of its divisions being as 28 : 60.

If, as is usual, several kinds of ores are to be smelted together, they should, for convenience, be subjected to a preliminary mixing, so as to reduce them to three only. Of these, one should have *less* and another *more* iron than is required in the final charge, and one should be acid and another basic after the correction for the ash from the coke has been made. Or one of the three may be a limestone or a siliceous flux ; it need not necessarily contain iron.

Then let it be required to have  $n$  parts of iron per hundred of the charge, and let  $a_1, a_2, a_3$  be percentages of iron in the ores, and  $b_1, b_2, b_3$  percentages of deficiency (or excess) of silica in the same, and  $x, y, z$  the number of parts required of the component ores per hundred of the charge.

Thus—

FeO.		Silica.
$x[a_1$	+	$b_1]$
$y[a_2$	-	$b_2]$
$z[a_3$	$\pm$	$b_3]$

Then—

$$(1) \quad x + y + z = 100$$

$$(2) \quad \frac{xa_1 + ya_2 + za_3}{100} = n$$

$$(3) \quad xb_1 - yb_2 \pm zb_3 = 0$$

Solving these simple equations, the number of parts of each component required to satisfy the desired conditions of the charge is at once found.

If it is desired to produce a more acid or a more basic slag, it is only necessary that the scale  $b$  be replaced by one the length of whose gradations are one-half (for bisilicate slag) or twice (for subsilicate slag) that of the normal scale.

A simpler form of the rule can be made by drawing the lines A B, A C, A D, A E, as before, upon a sheet of card, and then

setting out a scale of equal parts upon the datum line A B, and providing a loose strip of card, one edge of which is graduated to the same scale, taking care, in using the scale, to keep it at right angles to the line A B. This is, in fact, the equivalent of a set of Prof. Balling's diagrams, reduced to one scale, and brought to a common centre.

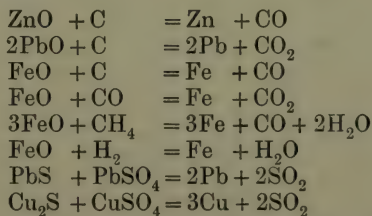
Mr A. Wingham<sup>1</sup> has also devised an excellent slide rule for the same purpose as the foregoing appliance, and by it the additions, as well as the multiplications, are mechanically performed, provision being made for all the ordinary constituents of slags.

**Classification of Metallurgical Processes.**—Metals may be extracted from their ores and from metallurgical products by the following methods:—

1. By *liquation*—that is, a separation of the easily fusible metals or metallic compounds from the infusible ones, or the gangue, at a low temperature, by taking advantage of the different melting-points. Bismuth and sulphide of antimony are thus obtained.

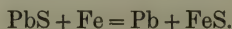
2. By *distillation* and *sublimation*—that is, heating the ore until the metal is driven off in the form of vapour, and condensed in a liquid or solid state. Mercury is extracted from its ore by distillation, and arsenic is obtained by sublimation. Mond's unique process for nickel extraction might also be regarded as falling under this heading, the nickel being "distilled" off as the gaseous carbonyl ( $\text{Ni}(\text{CO})_4$ ), which is subsequently decomposed and the nickel deposited.

3. By reduction of metallic oxides at a high temperature. In the case of metals possessing a slight affinity for oxygen, the reduction may be effected by merely heating the oxide, whereby it splits up into metal and oxygen. The reduction is usually effected by heating the oxides with carbon or other substances possessing a greater affinity for oxygen than is possessed by the metal. In addition to solid carbon, the substances used are carbonic oxide, marsh-gas, and hydrogen, as well as sulphur in the reverberatory-furnace processes for extracting copper and lead. The reactions are shown by the following equations:—



<sup>1</sup> *Journ. Iron and Steel Inst.*, i., 1892, p. 253.

4. By decomposing metallic sulphides by means of iron at a high temperature. Lead and antimony are extracted from their ores in this way, the equation in the case of lead being—



5. By extraction by means of molten lead, as in the treatment of certain argentiferous mattes.

6. By extraction by means of molten zinc, as in the extraction of silver and gold from lead by the Parkes process.

7. By extraction by means of mercury in the cold—*i.e.* by *amalgamation*. It is used for extracting silver and gold from their ores, the mercury being subsequently driven off by heat.

8. By extraction in the wet way and subsequent precipitation, as metal or as oxide or sulphide. In some cases the compound is dissolved in acids, as in the separation of silver from gold, and in the extraction of copper and nickel. In other cases the metal is first converted into a chloride, which is dissolved in a solution of salt or of sodium hyposulphite, as in the extraction of silver by Augustin's process, or the metal is converted into a sulphate, which is dissolved in water, as in Ziervogel's process. The extraction may also be effected by treating oxides with salts, as in the Hunt and Douglas method of extracting copper,



9. By electrolysis, as in the deposition of copper, silver, and gold.

10. By means of the electric furnace.

11. By the action of oxidisers on metallic salts, as in the precipitation of gold from its solution as chloride by ferrous sulphate.

12. By crystallisation, Pattinson's silver extraction method.

13. By the reducing action of some other substance as Al in aluminothermic processes, Si, Ca, etc., being other examples.

**Roasting and Calcination.**—These terms are frequently used indiscriminately to indicate the operations of expelling water, carbonic anhydride, or sulphur from the ore by heating it to a temperature below its melting-point. The term "calcination" should be confined to the application of heat in the expulsion of carbonic anhydride or volatile matters, whilst the term "roasting" should be used in all cases where a chemical change is involved, resulting in the addition of an element.

Roasting is one of the most important of metallurgical processes. In the treatment of almost all ores it is required as a preliminary process to render them more porous and more suitable for the subsequent smelting, the success of which depends on how the roasting is effected.

The various methods of roasting are dealt with in the other volumes of this series,<sup>1</sup> and more exhaustively by Peters.<sup>2</sup> They

<sup>1</sup> Rose, *Metallurgy of Gold*; Collins, *Metallurgy of Silver and Lead*.

<sup>2</sup> Peters, *Copper Smelting*.



may be roughly divided into those which treat the materials (1) in lumps or (2) in powder. For the furnaces employed see next chapter.

There are several kinds of roasting. An *oxidising* roasting is one in which the metalliferous substance is oxidised by heating it in contact with air. A *reducing* roasting consists in heating the substance in a reducing atmosphere. When it is required to obtain chlorides instead of oxides, the material is roasted with salt. This operation is termed a *chloridising* roasting. It is especially important in the treatment of silver ores. Under the action of a high temperature the salt acts on the sulphates present and forms chlorides. Its action may also be due to the formation of chlorine by the action of silica and sulphuric anhydride on the salt, or to the evolution of hydrochloric acid, due to the presence of moisture in the atmosphere in which the material is being roasted. *Sulphating* roasting, or roasting in such a manner that sulphates are formed. It necessitates a low temperature and a limited supply of air.

Several processes which may be considered under the general term *lime roasting* have recently come into prominence, owing to the success they have met with in rapidly desulphurising galena and leaving it in a very suitable physical condition for subsequent blast-furnace treatment. Of these processes the Huntington-Heberlein comprises two operations: (1) heating slowly in a reverberatory furnace a mixture of galena and lime, 6 to 15 per cent. being used according to the amount of sulphur in the ore; (2) transferring the partially desulphurised hot mixture into a pear-shaped vessel made of sheet iron, and blowing air through, with the result that nearly all the sulphur is oxidised, and the temperature is raised sufficiently to agglomerate the mass. The Carmichael-Bradford process consists of feeding a mixture of galena with 10 to 35 per cent. of dehydrated gypsum into a converter on the top of a small bed of glowing coal kept incandescent by a gentle blast. The Savelsberg process resembles the latter process, but limestone is used instead of gypsum. A modification of these processes, known as pot-roasting, has been introduced into some American works, and is worked on charges low in lead and nearly free from limestone. The apparatus consists of a cast-iron kettle, 8 feet 6 inches in diameter, with a detachable hood. The kettle has a cast-iron plate near the bottom, drilled with  $\frac{3}{8}$ -inch holes. A barrowload of ashes is first charged, then follow 1 to 2 tons of hot roasted ore, used to ignite the remaining 8 to 9 tons of charge. The ore mixture is made up to contain Pb 7-10,  $\text{SiO}_2$  30, S 20-25. The remaining 8 to 9 tons are slightly moistened and added to the previously ignited charge, and the blast kept on until the process is finished.

**Oxidising Agents.**—Atmospheric air is the simplest source of oxygen; it is employed at the ordinary pressure or at a pressure

of several atmospheres, for the temperature of combustion increases with the pressure.

Water is an active oxidising agent in the case of certain metals which have a strong affinity for oxygen, but in other cases its oxidising action is sensible only at a high temperature. The decomposition of water absorbs much heat, and aqueous vapour can therefore be employed only as an oxidising agent when its cooling effect is desirable. Aqueous vapour is also used for separating zinc from lead. In passing steam over sulphides of oxidisable metals at a red heat the sulphur is eliminated as sulphuretted hydrogen, while the metal is oxidised. This reaction is employed in the roasting of sulphides of iron, and in the treatment of sulphides, arseno-sulphides, and antimonio-sulphides of copper and silver.

Metallic oxides are frequently used as oxidising agents. Oxides of manganese, iron, and lead are those most generally employed. Oxide of copper is used more rarely. Manganese peroxide is occasionally useful in the oxidation of impurities in metals. Ferrous oxide, or ferrous silicate, acts as a carrier of atmospheric oxygen. When ferrous silicate, containing less than 30 per cent. of silica, is exposed in a molten state to the action of air, the iron in excess gradually becomes oxidised, and crystals of magnetic oxide are formed. These render the silicate less fusible, and fall by their superior density to the bottom of the mass. Sometimes, as when such a slag covers a bath of impure metal, the magnetic oxide thus formed gives up its excess of oxygen to the elements in the metal to be refined, and again becomes ferrous oxide, and thus acts as a carrier of atmospheric oxygen to the carbon which has to be oxidised. An illustration of this is afforded by a stage of the puddling of iron, a process which is conducted in the presence of a layer of ferruginous cinder.

Lead oxide is an energetic oxidising agent on account of its being readily reducible to the metallic state. It is, however, expensive, and yields but 7 per cent. of oxygen. Lead oxide and lead sulphide, when heated together, give metallic lead—



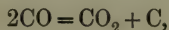
Oxides of copper and antimony serve as oxidisers in the treatment of these metals. In heating together the sulphide and oxide of copper, copper is obtained. Potassium and sodium nitrates are employed in refining silver and antimony, and in the "Heaton" process sodium nitrate was employed to convert phosphorus in certain varieties of pig-iron into sodium phosphate.

Metallic sulphates are often used as oxidising agents, the sulphate oxidising the sulphide and reducing the metal. In the case of iron in the blast furnace, carbonic anhydride also acts as an oxidiser.

**Reducing Agents.**—When a metal is separated from a state of chemical combination, it is said to be reduced, and the process of separation is termed *reduction*. The agents employed for this purpose are mainly carbon and hydrogen, or their compounds. Occasionally, however, the metallurgist makes use of iron, manganese, lead, aluminium, calcium, or of sulphides and arsenides. The efficacy of a reducing agent depends on the absence of oxidised or inert elements. Thus, on account of the water and oxidised compounds they contain, wood, peat, and lignite are less energetic as reducing agents than coal. Similarly, coals rich in carbon are more valuable as reducing agents than coals rich in oxygen.

Carbon can take up  $1\frac{1}{3}$  or  $2\frac{2}{3}$  of its weight of oxygen according to the oxide in whose presence it is used, to the temperature at which the reduction is effected, and to the relative proportion between the oxygen to be removed and the carbon employed. In the first case carbonic oxide is formed, and in the second carbonic anhydride. The reduction of metals, of which the oxides are easily reduced, such as lead and copper, is complete even if carbonic anhydride alone is formed. In the case of iron, however, total reduction is not possible unless carbonic oxide is present in excess, on account of the oxidising action of carbonic anhydride. Indeed, a mixture of equal volumes of carbonic oxide and carbonic anhydride will not reduce iron oxides below ferrous oxide. This is also true of manganese oxides.

Reduction by solid carbon is slow, and is effected merely by cementation, that is, by a gradual transmitting action, if carbonic oxide is not formed. This gas is the most important reducing agent. It penetrates to the centre of the oxidised substance, absorbs its oxygen, and is converted into carbonic anhydride. In this way 1 part by weight of carbonic oxide gives 1.57 parts of carbonic anhydride. Besides this, Gruner<sup>1</sup> and Sir Lowthian Bell<sup>2</sup> have shown that, even at low temperatures, carbon, in the presence of iron, separates out from carbonic oxide,



and has a powerful reducing action. Hydrogen is a powerful reducing agent, but is only used incidentally, or as water-gas.

In addition to the above-mentioned reducing agents, metals and metalloids are sometimes used to remove oxygen. Thus, iron deoxidises the salts and oxides of copper, of lead, and of mercury, sodium liberates the metals magnesium and aluminium from their haloid salts, and aluminium liberates the metals chromium, manganese, etc. from their oxides. Sulphides and arsenides are also employed. Thus, sulphides of iron and zinc separate copper

<sup>1</sup> *Ann. de Chim. et de Phys.*, 4th Series, vol. xxvi. (1872), p. 5; *Traité de Métallurgie*, vol. i. (1875), p. 172.

<sup>2</sup> *Chemical Phenomena of Iron Smelting*.



from certain slags. Silicates of iron and zinc are formed, while sulphur retains the copper in the regulus.

**Chemical Agents.**—Certain sulphurising agents are employed in metallurgical processes. These are specially useful in the treatment of silver and copper. The agents are iron or copper pyrites, barium or calcium sulphates, and, less frequently, alkaline sulphides. Nickel and cobalt behave with regard to arsenic as silver and copper do in the case of sulphur. These metals may be protected, by means of their affinity for arsenic, from the scori-fying action of silicates.

Chlorine is largely used in the treatment of gold and silver ores. It is employed in the gaseous state as an aqueous solution, or in the form of alkaline hypochlorites. The perchlorides of iron, copper, and mercury act as chloridising agents by being converted into lower chlorides. They are obtained usually by the direct action of hydrochloric acid on peroxides. Iodine in the form of iodide is used in the metallurgy of silver, and bromine in that of gold.

The agents employed for effecting the solution of metallic substances are very varied. The most important solvent is water, which is used for dissolving sulphates of iron, copper, zinc, and silver, and chloride of gold. Other salts are dissolved by salt solutions; thus, chloride of silver is dissolved by an aqueous solution of sodium chloride, or hyposulphites of sodium or calcium. The use of very dilute solutions of potassium cyanide in the extraction of gold<sup>1</sup> has assumed great importance, and numerous patents for its production have been secured;<sup>2</sup> sodium cyanide, also, is now largely used in the treatment of gold and silver ores. Metallic oxides are dissolved by acids; gold and platinum are dissolved by aqua regia; and in the amalgamation of gold and silver, mercury is the solvent employed.

In metallurgical processes there are scarcely any limits to the use of ordinary chemical reagents beyond those imposed by the price of the material.

<sup>1</sup> Rose, *Metallurgy of Gold*.

<sup>2</sup> *Mineral Industry*, 1894, p. 79.



## CHAPTER IX.

### FURNACES.

**Materials used in the Construction of Furnaces.**—In addition to the ordinary building materials used for the exterior portions of furnaces, refractory bricks and materials are required for the interior where a high temperature and the scouring action of metallic oxides have to be resisted.

There are three classes of refractory materials :—

1. *Acid*—Dinas rock, ganister, and most fire-clays.
2. *Basic*—Dolomite and magnesite.
3. *Neutral*—Bauxite, chrome-iron ore, graphite, and a few fire-clays.

**Acid Refractories.**—Siliceous materials are most generally employed, as in the great majority of cases all that is required is a material capable of resisting high temperatures, and also mechanically strong under great variations of temperature. It is only when the chemical reactions involved are such that a siliceous lining would interfere or be fluxed away that neutral or basic linings are used. For roofs, side walls, and all those parts of the furnace which do not form part of the hearth or “laboratory,” siliceous bricks are almost universally employed in all metallurgical works. Thus all copper-smelting furnaces, all reheating and annealing furnaces, whether for copper, steel, or other metals, ore-roasting furnaces, many steel-smelting furnaces, and practically all blast furnaces, are built with some kind of siliceous fire-bricks, sometimes nearly pure silica, when very high temperatures have to be resisted, at other times of different kinds of fire-clay.

The question of contraction and expansion is an important consideration in selecting a fire-resisting material, as some expand much more than others, and for certain parts of a furnace this may be a serious disadvantage, while for others it is of no consequence, and may even be an advantage.

These materials may be used either in the natural state or as bricks. Of the natural materials, sandstones are most largely employed, the best varieties being those in which the quartz

grains are cemented by a siliceous material. In the form of quartz, silica is able to resist all temperatures up to that of the oxyhydrogen blowpipe. Coarse-grained sandstones, such as millstone grit, are frequently advantageously used. The Dinas rock found in the Vale of Neath, South Wales, is an example of this type. It usually contains 98 per cent. of silica. The pulverised rock is mixed with a little lime or clay to make it cohere, and is pressed into bricks. These resist a very high temperature, and are especially useful for the arches of reverberatory furnaces, as they expand with heat. Their composition, however, does not enable them to resist the action of metallic oxides. In steel-melting furnaces, where Dinas bricks are used for roofs, the tie-rods must be slackened as the heat increases, and tightened when the furnace subsequently cools. Ganister is a siliceous material, somewhat similar to the Dinas stone, found in the lower coal-measures of Yorkshire; most fire-clays are also siliceous, that is, they contain an excess of silica.

Fire-bricks are mostly made of fire-clay, mixed with quartz or burnt clay. The admixture of graphite is not usual for fire-bricks, but is used for refractory crucibles in which metals and alloys are melted.

Fire-clays consist essentially of hydrated aluminium silicates, having the following composition:—

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{H}_2\text{O}$ .
55 to 65	22 to 35	10 to 15

When lime, magnesia, potash, or soda are present in quantities exceeding 1 per cent. the clay becomes fusible. In aluminous clays less than 0·7 per cent. of these oxides does not depreciate their refractory value, but, as a rule, a small amount of these oxides or of ferrous oxide is sufficient to condemn a clay. Thus ordinary shale fuses at a comparatively low temperature, on account of its large percentage of alkaline oxides and ferrous oxide.

The plasticity of clays depends upon the fineness of the particles and the amount of water present. Plasticity is tested for by means of standard needles, the degree of penetration being noted under definite pressure. After being calcined, clays cease to be plastic when moistened, on account of the molecular alteration brought about by the calcination. Fire-clays contract when heated, even after all their combined water has been driven off, but heating up to 100° does not affect plasticity; it merely drives off the hygroscopic water. The quality of the clay is largely dependent upon the free silica it contains. Windsor fire-bricks, useful when the temperatures are not high, are made of a mixture of sand and fire-clay in equal proportions.

The mortar employed for setting fire-bricks is prepared from

the same materials as the bricks themselves, or from good clay. Lime mortar must not be employed for fire-bricks or fire-clay.<sup>1</sup>

Sexton<sup>2</sup> gives details as to refractory materials, while excellent articles by Ferry<sup>3</sup> deal with the principles underlying the successful manufacture of fire-brick.

**Basic Refractories.**—These are now very largely employed in the manufacture of steel, both for lining Bessemer converters and open-hearth furnaces. There are only two materials used to any extent, viz. burnt dolomite, known as “basic material,” and magnesite. The use of a basic lining is essential both in the Bessemer and open-hearth process when a phosphoric pig-iron has to be used, as without it the phosphorus present cannot be removed. Dolomite containing as little silica as possible, preferably not exceeding 1·5 per cent., is calcined at a very high temperature to completely expel the CO<sub>2</sub> and thoroughly shrink it, after which it does not very readily absorb moisture, and if protected from the direct action of the air, can be transported considerable distances by rail without serious deterioration. After calcination it is ground fairly fine, and either mixed with tar and moulded into bricks or used as a ramming for making the furnace lining: in the case of open-hearth furnaces it is more usual now not to mix it with tar, but to frit it on to the furnace-bottom in the dry state.

Magnesite forms a still better refractory lining than basic material, and magnesite bricks are now very largely used. The magnesite is “dead burnt” and then moulded into bricks, sufficient fusible material being added to frit the magnesia together and form a hard brick which will bear transport. These bricks are much more expensive than “basic material,” weight for weight, but they last so much longer that for certain parts of steel furnaces the extra cost is more than compensated for by the longer life.

Lime, from a chemical standpoint, is just as good as basic material; but although it is extremely refractory, no one has yet succeeded in producing a satisfactory mechanical brick, as, owing to the readiness with which it becomes hydrated, the bricks rapidly disintegrate.

**Neutral Refractories.**—These are not very largely used, although in some special cases the hearth or “crucible” part of the furnace is lined with them. Thus bauxite has been used for resisting the action of metallic oxides, but it is not very refractory as compared with basic materials. It consists essentially of hydrated alumina, containing varying quantities of oxide of iron, but only the purest varieties are suitable for the manufacture of

<sup>1</sup> Snelus, *Journ. Iron and Steel Inst.*, 1875, p. 513.

<sup>2</sup> Sexton's *Fuel*.

<sup>3</sup> *Mineral Industries*, vol. iv., 1895, p. 113; *ibid.*, vol. vii., 1899, p. 129.



bricks, and it should approximate to the following percentage composition :—

$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{SiO}_2$ .	$\text{H}_2\text{O}$ .
85 to 90	1.0 to 3.0	2.0 to 4	10 to 15

Another neutral material which has been used to a limited extent is chrome-iron ore, which has been found to be useful to form a neutral joint between basic and acid materials; various attempts have also been made to use it as a lining for open-hearth steel furnaces, but this has not been successful. Oxides of iron have also been used for the hearths of different furnaces, and also the slags produced in various operations, many of which may be regarded as neutral bodies.

Graphite in admixture with aluminous fire-clays has also been used for some special purposes, but, apart from the manufacture of crucibles, has never been largely employed.

**Crucibles.**—For special metallurgical purposes, crucibles, as in the case of cast steel, and retorts, as in case of zinc and arsenic smelting, are used.

Crucibles are required to resist (1) high temperatures; (2) alternating temperatures; and (3) the corroding action of metallic oxides. They must also not be brittle or “tender” when hot. They may be made of clay, magnesia, graphite, gas-carbon, and many other materials, according to requirements. When made of clay, two-thirds are raw clay and one-third is burnt clay, or pulverised material obtained from old but clean pots. By this addition, contraction on drying is avoided.

In order to test fire-clay, a piece is fashioned with sharp angles, dried, and exposed to a white heat in a muffle; it is then examined to see if the edges have fused. A similar test should be made in a reducing atmosphere, the test-piece being placed in a crucible packed with charcoal.

In order to test the resistance of a crucible to corrosion, it may be half filled with copper, which is then melted, and a little borax inserted so as just to form a ring round the edge of the molten metal and yet leave the centre free for oxidation. The borax will absorb the oxide and rapidly corrode the crucible unless it be of excellent quality. The behaviour of the crucible under the weight of the copper melted indicates the other qualities of the crucible. In selecting clay for crucibles, special care must be taken that neither iron pyrites nor more than a minute percentage of potash or soda is present. A small quantity of lime is of less importance.

The so-called plumbago crucibles are made of clay and graphite, in the proportion of 51 of the former to 49 of the latter. Only certain varieties of graphite can be used for crucible-making, the texture being of great importance: the suitability can only be determined by experiment. The graphite is picked, ground, sifted, and mixed with the fire-clay, and left for some time to



"mellow" after it has been kneaded damp. The crucibles are moulded, dried, and then burnt in kilns. Obviously, an oxidising atmosphere must always be avoided. In order to prevent absorption of moisture and salts, as in cases of shipment, and to enable rapid alterations of temperature to be better withstood, the finished crucibles are dipped in milk of clay, dried, glazed, and then dipped in tar. Crucibles made in this way by the Battersea Crucible Company will stand forty meltings of gold without sensible deterioration.

The pots used in the chlorination process for parting gold and silver are soaked in borax solution, dried, and heated. The borax then melts and clogs the pores, and prevents the escape of the silver chloride, which is very fluid.

**Classification of Furnaces.**—The words *hearth*, *forge*, and *furnace* are applied to structures in which ores or metals are submitted to high temperatures. A furnace is composed of an interior part, of fire-resisting materials, and an exterior part, built for the purpose of consolidating the interior structure. Furnaces may be divided into two classes—(1) those in which the charge and solid fuel are in intimate contact, there being no independent hearth or fireplace; and (2) those in which the solid fuel and ore are kept separate, the fuel being burnt in an independent hearth. The first class of furnaces may be subdivided, according to their height and construction, into *hearths* and *shaft-furnaces*; the former are appliances that usually do not work continuously, whilst in the shaft-furnace the action is continuous. The second class is subdivided into (a) *reverberatory furnaces*, a group in which gas-furnaces may be included; and (b) *retort-furnaces*. In the former, the charge only comes in contact with the flame of the fuel, whilst in the retort-furnaces it does not come into contact with the combustible gases of the fuel at all, but is separated from them by walls that merely transmit the heat. These walls usually form part of separate closed vessels, crucibles, muffles, or retorts, but occasionally they are part of the furnace itself, as in the case of the Bessemer converter, which may be described as a vessel usually pear-shaped, in which the impurities contained in the metal treated constitute the fuel, which is burnt by a forced current of air. Furnaces may be further divided into those worked by means of a natural current of air, and those worked by a forced current of air. The classification of furnaces may then be summarised thus:—

### I. HEARTHS.

(a) Worked by means of a natural current of air. (1) Roasting-hearth (piles, stalls, pits, kilns); (2) Liqutation-hearth.

(b) Worked by means of a forced draught (the smith's forge, iron refinery).

## II. SHAFT-FURNACES.

- (a) Draught-furnaces (iron ore calciners).
- (b) Blast-furnaces (iron blast-furnaces, Raschette-furnace, Pilz-furnace, cupola-furnace).

## III. REVERBERATORY FURNACES.

- (a) Worked by means of a natural draught (puddling-furnace).
- (b) Worked by means of a forced draught (cupellation-furnace).
- (c) Automatic reverberatory furnaces (rake-calciners).

## IV. CLOSED-VESSEL FURNACES,

in which may be included various forms of crucible-, tube-, and retort-furnaces, converters, etc., and which may be divided, according to the process carried out in them, into—

- (a) Smelting-furnace (ordinary assay-furnace).
- (b) Oxidising-furnace (copper and steel converter).
- (c) Liquation-furnace (bismuth).
- (d) Distillation-furnace (zinc, mercury).
- (e) Sublimation-furnace (arsenious acid).
- (f) Cementation-furnace (cement steel).

## V. ELECTRICAL FURNACES,

in which the combustion of carbon need not, even indirectly, produce heat.

**General Principles.**—Whether natural or forced draught is used, the general principles involved in fuel combustion apply. The fuel employed in either case may be the same, but the products of its combustion may be widely different. The form and dimensions of the furnace will obviously give rise to very varied results; on them depends the amount of fuel that can be burnt in a given time, and the degree of perfection of the combustion that can be attained, the temperature actually engendered being dependent on the calorific power of the fuel. In a furnace without an independent hearth, the most important part is that in which the work is principally done. This may be conveniently localised as the zone of combustion. Thus, as Gruner expresses it, for a given fuel burnt in a certain way, the heat developed will simply be proportional to the weight of fuel burnt, whilst the temperature depends on the rapidity of combustion—that is, on the ratio between the volume of the zone of combustion and the weight of coal or coke burnt in an hour. The smaller this ratio, the higher the temperature will be.

In order to show how varied the conditions may be, the following two cases may be cited:—(1) An ordinary coal-fired

Gjers calcining kiln, such as for years has been almost universally used in the Cleveland district for calcining ironstone with a natural draught of air. The height of the furnace is 33 feet, and its total internal capacity is 8000 cubic feet; but the work of the furnace—namely, that of driving off carbonic anhydride and moisture from an iron ore—is not confined to a limited zone; indeed, the volume of this zone of combustion may be taken to be about 1400 cubic feet. Compare this with (2) a modern blast-furnace, such as that used at the present time in Middlesbrough. The height of the furnace is about 76 feet, and its output may be 4000 to 5000 tons per month, or about 140 to 160 tons of pig-iron in twenty-four hours. In this case the air previously heated is driven in, a course which is necessary in order to overcome the resistance of the superincumbent and partially fused mass of ore, fuel, and flux, and the result is that the combustion of the fuel is more or less limited to an intensely hot zone of combustion.

Furnaces with independent hearths are usually reverberatory furnaces, although there are cases in which vat-shaped furnaces are supplemented by fire-grates, which are usually symmetrically arranged round the base. The object of isolating the fuel from the ore is to prevent chemical action of a kind that is not wanted, and generally to enable the nature of the products of combustion admitted into the furnace to be controlled. It would be useless, for instance, to admit torrents of carbonic oxide into a furnace where an oxidising action was wanted, and, conversely, the predominance of an atmosphere of carbonic anhydride would be fatal to a reducing action.

It is usual to consider a reverberatory furnace as consisting of a grate to hold the fuel, and the "laboratory" portion in which a given operation is conducted. The nature of the operation may be infinitely varied, and the temperature of the laboratory may vary from the dull red heat required for roasting pyritic ores to the intense heat required for melting steel. Obviously, the dimensions of the grate in relation to those of the laboratory will vary considerably according to the nature of the operation to be carried on in the furnace.

**I. Hearths.**—A hearth is a low furnace in which the material to be treated is exposed to the direct action of solid fuel. Heaps, stalls, and kilns for roasting ore are also included in this category, as the action of the fuel is the same. Consequently, hearths are not necessarily enclosed furnaces, but may exist without the aid of any brickwork at all. The pyramidal heaps, in which the roasting of copper ores is effected, are free or unwalled, about 30 feet square at the base, and built upon level ground. A bed of wood, about 1 foot in thickness, is formed, and on this alternated layers of ore and charcoal are piled to a vertical height of 10 feet. Some ironstone from the coal-measures may be



roasted in heaps without the addition of fuel. The proportion of bitumen in the copper shale of Mansfeld is almost sufficient for its calcination. With sulphuretted ores, a bed of fuel is used, the burning sulphur keeping up the roasting temperature. Peters<sup>1</sup> describes the large-scale American methods of heap-roasting. The liquation-hearths formerly employed for separating easily fusible constituents out of metallic mixtures also belong to this class.

Hearths worked by means of a forced current of air may be employed for melting, or for heating a substance to a very high temperature without altering its state of aggregation, as in welding and forging metals that are not readily fusible.

An example of this class of hearth is the refinery formerly largely used in the manufacture of wrought iron. It consists of a rectangular hearth, provided with inclined tuyères, through which air is blown upon the surface of the molten iron, so that the silicon in the iron is oxidised, forming with a portion of the iron a fusible ferrous silicate. This process is confined to a few localities making special qualities of wrought iron.

Further examples are afforded by the shallow hearths used for lead-smelting. In the north of England a furnace of this kind, known as the *ore-hearth*, is sometimes used. It consists of a cubical chamber about 22 inches side, lined with cast iron. In the back wall is fixed a tuyère for the introduction of the blast. In front is the work-stone, which is placed at a slight inclination to the bottom of the hearth. The melted lead flows from the hearth down an oblique channel in the work-stone to a lead pot placed before the work-stone. The operation lasts about twelve hours, the production being 1 to 1½ ton of lead. Peat was formerly used as fuel, but it has now been abandoned, and coal is generally employed.

In hearths and kilns of this class the introduction of cold material renders the combustion of the fuel, whether gaseous or solid, more or less imperfect, so that the products of combustion contain an inordinate amount of unburnt gases, especially of carbonic oxide. As a rule, in a kiln the position of the zone of combustion is fixed, but it occurred to Hoffmann,<sup>2</sup> a German architect, to devise a kiln in which the position of the zone of combustion can be varied at will, and he thus succeeded in effecting a considerable economy of fuel. In an ordinary kiln there is a continuous ascending column of gas, and a descending column of solid material. In the Hoffmann and kilns of this type, on the other hand, the solid material remains stationary, while the gaseous current alone moves. The kiln may be either circular or oval in section. This is shown in fig. 148. It consists of a circular tunnel, *MM*, which can be divided into any number

<sup>1</sup> Peters, *Copper Smelting*, chaps. vi. and vii.

<sup>2</sup> *Annales des Mines*, 6th Series, vol. xx. (1871), p. 325.



of compartments, twelve or sixteen being the usual number. These compartments are, however, in direct communication with each other except at one point, where an iron plate, *pp*, placed across the tunnel, interrupts the continuity. This plate may be inserted through the roof of the tunnel down grooves, *nn*, provided for its reception, in the walls. Each space between two

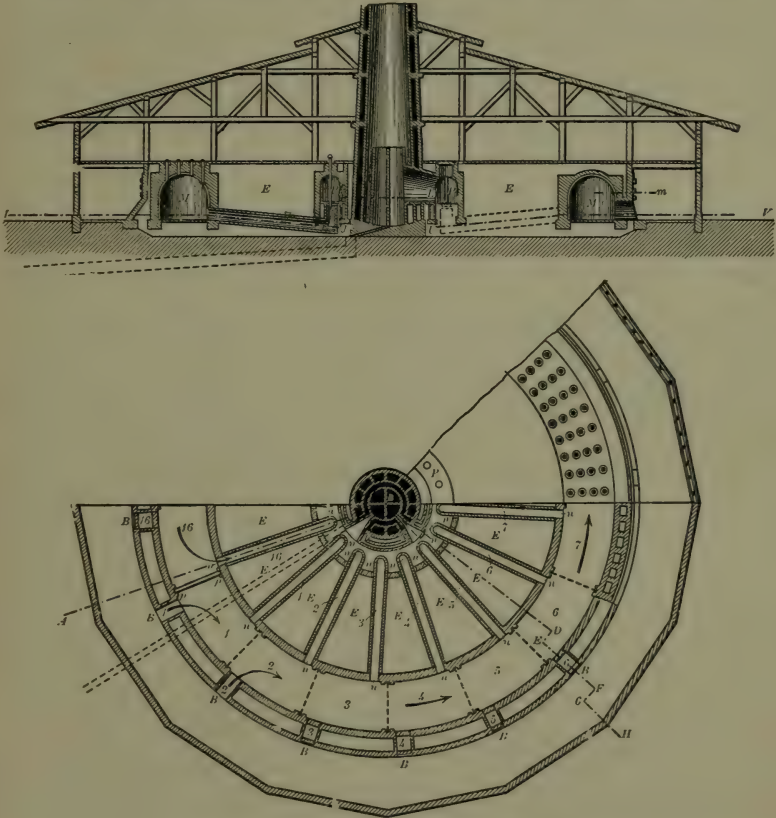


FIG. 148.

sets of grooves is provided with an internal flue,  $E_1 E_2$ , which, by the removal of a damper, can be placed in communication with a central chimney, and each space has also a door, *BB*, in the outer wall. Only two of these doors are open at a time. The whole of the tunnel is kept full of material (ores to be calcined, or bricks to be burnt), except one compartment, which is always empty. The position of the empty compartment varies from day to day. Let the plate occupy the position, *pp*, shown

in fig. 148. The newest material has been charged in behind it into compartment 16. Air enters in front of it through the open door of the empty compartment No. 1, and through the door, also open, of the next compartment, which contains finished material that has been longer in the furnace than the rest, and has but little heat to give up to the incoming current of air. This current is drawn by natural draught round the entire tunnel, and can only enter the chimney through one or more of the flues that have been opened behind the plate. After an interval of twenty-four hours from the last charging, the position of the iron partition is shifted to the next groove to the right, the compartment No. 1 is filled, and the one, No. 2, in front of the plate is emptied. Thus new material is continually kept behind the plate, and finished material in front of it. Air entering comes in contact with material which gradually increases in temperature, for it will be obvious that the position of the hottest part of the furnace

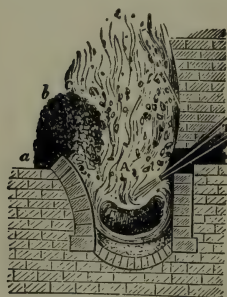


FIG. 149.

must be continually travelling round the circle, and that in a number of days, corresponding with the number of compartments, the zone of combustion will have travelled completely round the circuit. The air and the material to be treated enter and leave the furnace in a cold condition, so that there can be no waste of heat, provided that the adjustment of the dampers in the flues through which the gases pass to the chimney is carefully effected. In order to remedy local irregularities of combustion, air may, if necessary, be ad-

mitted through suitable orifices in the roof.

The volume of each compartment may vary from 282 to 1765 cubic feet. In order to facilitate charging and to secure perfect uniformity of temperature, the height of the tunnel should not exceed 9 feet.

In Catalonia a low hearth, the Catalan furnace (fig. 149), is still occasionally to be met with. It is used for the production of malleable iron direct from the ore. It is made of blocks of cast iron and has a sandstone bottom. The tuyère is made of sheet copper. The blast is supplied by a water-blowing machine, or *trompe*, which may be made from a hollow tree trunk, 15 feet high, at the top of which is a water-box with a plug. The water falls down the pipe into the wind-box, carrying air with it, and causing a pressure of  $1\frac{1}{2}$  to 2 lbs. per square inch in the hearth.

**II. Shaft-furnaces.**—In most of the members of this group the fuel and ore are charged into a common receptacle, the major axis of which is vertical. Certain of them, as the kilns in which

limestone or ore is calcined, are worked by a natural current of air, the furnace itself forming a capacious chimney.

The form of these furnaces is very varied according to the nature of the ore and of the fuel employed. Furnaces of this kind may be egg-shaped, cylindrical, or conical. Small kilns with circular horizontal section effect the most uniform roasting, give rise to the least loss of heat by radiation, and wear well. The height is dependent on the size of the pieces and on the fusibility

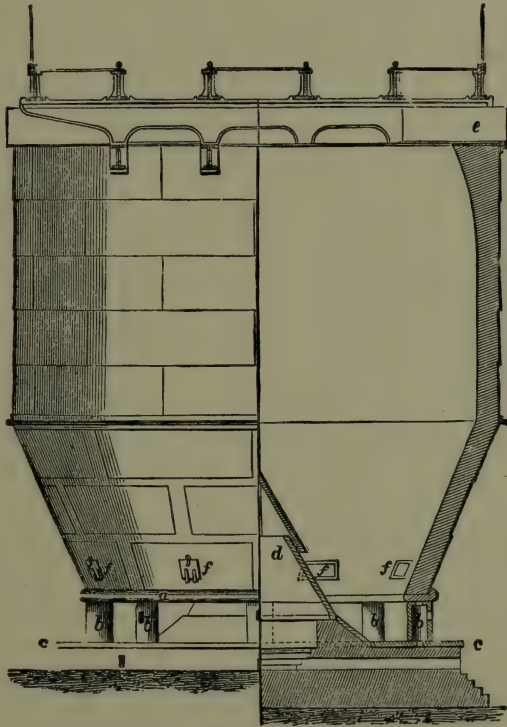


FIG. 150.

of the ore. The width is dependent on the quantity of ore to be roasted. In large kilns of circular section it is difficult to maintain a uniform temperature. Large kilns have consequently an elliptical or rectangular section. In the latter case the corners are rounded off.

The best examples of this type of furnace are afforded by the kilns employed for calcining iron ores. One of the best forms is that of Gjers (fig. 150), which is extensively used in the Cleveland district. The drawing, to the scale of 10 feet to the inch, shows



this kiln partly in elevation and partly in section. The body is of fire-brick cased with wrought-iron plates. The bottom of the brickwork rests on a cast-iron ring, *a*, and the whole is supported by cast-iron pillars, *b*, leaving a clear space between the bottom of the kiln and the floor. The latter is covered by iron plates, *c*, on the centre of which is fixed a cast-iron cone, *d*, 8 feet in height and 8 feet in diameter at the base. This causes the descending roasted ore to pass outwards. Fresh ore and coal are constantly being added from the filling gallery, *e*. Around the lower tier of plates are openings, *f*, which are usually closed by doors, but which serve for the admission of air or tools in case of the ore becoming clotted. These kilns are usually 33 feet in height, 24 feet in diameter at the widest part, and have a capacity of 8000 cubic feet. They calcine 1000 tons of iron ore per week, the consumption of coal amounting to 1 ton for 25 tons of ore.

The most important member of the group of furnaces without separate hearth is the blast-furnace. As its name implies, it is worked by a forced current of air supplied by blowing-engines. In former times charcoal was exclusively the fuel employed, whilst at the present time coke is mostly used. Raw fuel (coal or anthracite) is only adopted in special cases. The modern blast-furnace, in which coke is used as fuel, is 70 to 80 feet in height, some of the larger examples attaining to 100 feet. Charcoal blast-furnaces are considerably smaller. Formerly the blast-furnace was a heavy conical mass of masonry some 30 feet in height. It is now a much lighter structure, formed of a wrought-iron casing lined with brickwork. In order to distinguish it from the older forms, it is termed a cupola blast-furnace. In the upper opening, or throat, fuel, ore and flux are charged, being allowed to fall into the furnace, usually through some form of appliance for distributing the charge. In the lower narrow portion of the furnace, highly compressed air is forced through a number of horizontal nozzles or tuyères arranged in a circle. When the blast is previously heated, water-cooled tuyères are always employed, which consist of hollow truncated cones provided with an annular space all round, in which water freely circulates. In the space in front of the tuyères the combustion of the fuel is largely effected, this being already highly heated in its descent through the furnace, and a temperature of more than 2000° is obtained. The plane in the blast-furnace where the greatest diameter is reached is termed the *boshes*, and the cylindrical portion at the base is the *hearth*, in which the molten material collects. The top of the furnace is surrounded by a charging-gallery, and is usually covered in by an iron cup and cone, the latter of which may be lowered by a counterpoise and winch, or by a hydraulic cylinder, when material is to be charged in; the waste gases pass through a side tube, whence they are led to the stoves for



heating the blast, burnt under boilers, or used in internal gas-combustion engines. The stack is carried on an iron ring resting upon iron columns, the object being to have all the working parts of the furnace readily accessible, so that they can be repaired from time to time.

The hearth or crucible of the furnace is circular, and its capacity largely determines the output of the furnace. The bottom is made of refractory sandstone, carefully jointed. The tap-hole should be placed midway between two tuyères, so as to be cool and easy of access and on a level with the bottom of the furnace. The slag notch should be placed away from the tap-hole and at a certain distance below the tuyères. The iron is run into sand moulds, forming *pigs* about 3 feet long.

A large modern blast-furnace produces 75 to 200 tons of pig-iron in twenty-four hours, and in American practice a daily output of 400 to 500 tons is not unusual, whilst small charcoal blast-furnaces yield only 5 tons in the same time, and large ones up to 40 tons.

A convenient classification of blast-furnaces is that based on the ratio of the maximum diameter to the height. In this manner the following three classes may be distinguished:—

1. Squat furnaces, in which the height is less than, or equal to, three times the diameter,  $\frac{H}{D} < 3$ .

2. Ordinary furnaces, in which the ratio  $\frac{H}{D}$  varies between 3 and 4, but is usually about 3·5.

3. Elongated furnaces, in which the ratio  $\frac{H}{D}$  is greater than 4.

The following table gives comparative data of the dimensions and workings of ten blast-furnaces used for the smelting of iron, the outlines being shown in fig. 151.

	Cubic Capacity.	Total Height.	Diameter at Hearth.	Diameter at Boshes.	Diameter at Throat.	Daily Out-put.	Time in Furnace.	Fuel per Ton of Metal.
	cub. ft.	ft. ins.	ft. ins.	ft. ins.	ft. ins.	tons.	hours.	lbs.
1	30,000	85 0	8 0	28 0	19 0	70	150	2308
2	18,000	80 0	11 0	22 0	16 0	270	21	1863
3	15,000	75 0	11 0	20 0	15 4	175	24	2116
4	14,000	75 0	8 0	21 0	14 0	107	36	2130
5	8,824	73 8	9 6	15 6	11 9	142	20	1943
6	6,676	72 4	8 6	14 0	9 6	114	19	1697
7	2,000	50 0	5 6	10 0	5 6	48	8	1870
8	1,872	49 8	4 6	10 4	3 4½	24	10	1365
9	1,235	37 3½	5 8	8 4½	3 1½	24	4	1653
10	1,000	37 6	5 6	7 9	3 0	20	7	1585

In the first six furnaces coke is the fuel employed, whilst char-

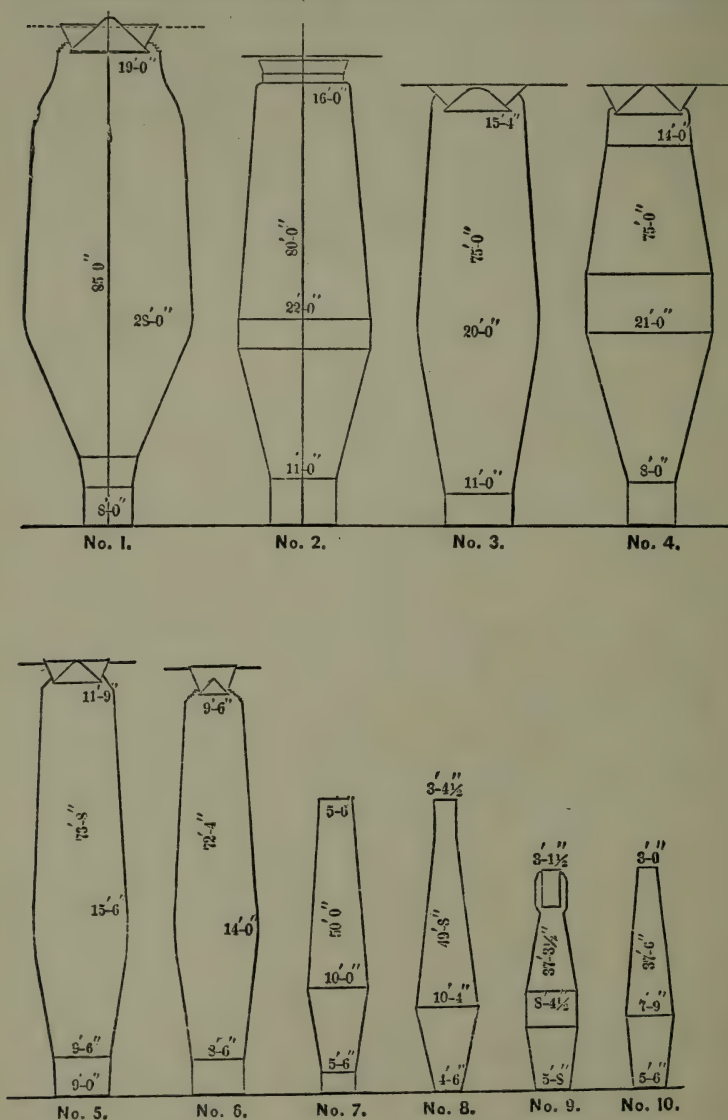


FIG 151.—Outlines of Iron Blast-Furnaces.

coal is used in the last four. The names and situations of the furnaces are: 1. Newport, England; 2. Edgar Thomson "F,"

Pittsburg, United States; 3. North Chicago, No. 6, Chicago, United States; 4. North Lonsdale, No. 3, Lancashire; 5. Union, No. 3 and No. 4; 6. Union, No. 2, Chicago; 7. Midland, Crawford County, Missouri, United States; 8. Treibach, Austria; 9. Ferdinand, Hieflau, Austria; 10. Wrba, Eisenerz, Austria. The first four of these furnaces belong to the second class, in which  $\frac{H}{D}$  is less than 4, whilst the last six are elongated furnaces in

which the ratio  $\frac{H}{D}$  is greater than 4. The following are examples of the first class, in which  $\frac{H}{D}$  is 3 or less than 3:—

	Name.	Cubic Capacity.	Height.	Diameter at Throat.	Diameter at Boshes.	Daily Output
		cub. ft.	ft.	ft. ins.	ft. ins.	tons.
11	Longwy, France .	14,656	65	13 6	23 0	40
12	Clarence (old type) .	6,003	50	7 10	16 6	30
13	Thornaby „ .	12,784	60	14 9	20 0	...
14	Ormesby „ .	40,984	90	15 9	30 0	...

In furnaces of this type the working is irregular on account of the contraction at the throat, which renders it difficult to apply any mechanical method of distributing the charge uniformly.

The student should refer to the excellent paper by Grenville Jones on “A Description of Messrs Bell Brothers’ Blast-Furnaces from 1844 to 1908”<sup>1</sup> for a well-illustrated historical account of the development of blast-furnace practice in this country.

A modern American blast-furnace is shown in fig. 152, in which an automatic charging apparatus is seen, which consists of an inclined girder tramway, on which there are generally two lines of rails, so that the weight of the ascending skip is balanced by that of the descending skip on the other line.

These skips are made of strong sheet steel, and carry about 2 tons. Arrangements are made by means of guide rails at the top of the tramway for the automatic tipping of the contents of the skip into the double cup and cone. The skips are filled from hopper-shaped bins which are arranged near the foot of the furnace hoist. Separate bins are provided for ores, coke, and limestone.

It was formerly the practice to allow the waste gases to burn

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1908, iii. p. 59.

at the throat of the furnace. Since the introduction of the hot blast, however, it has become usual to apply some arrangement

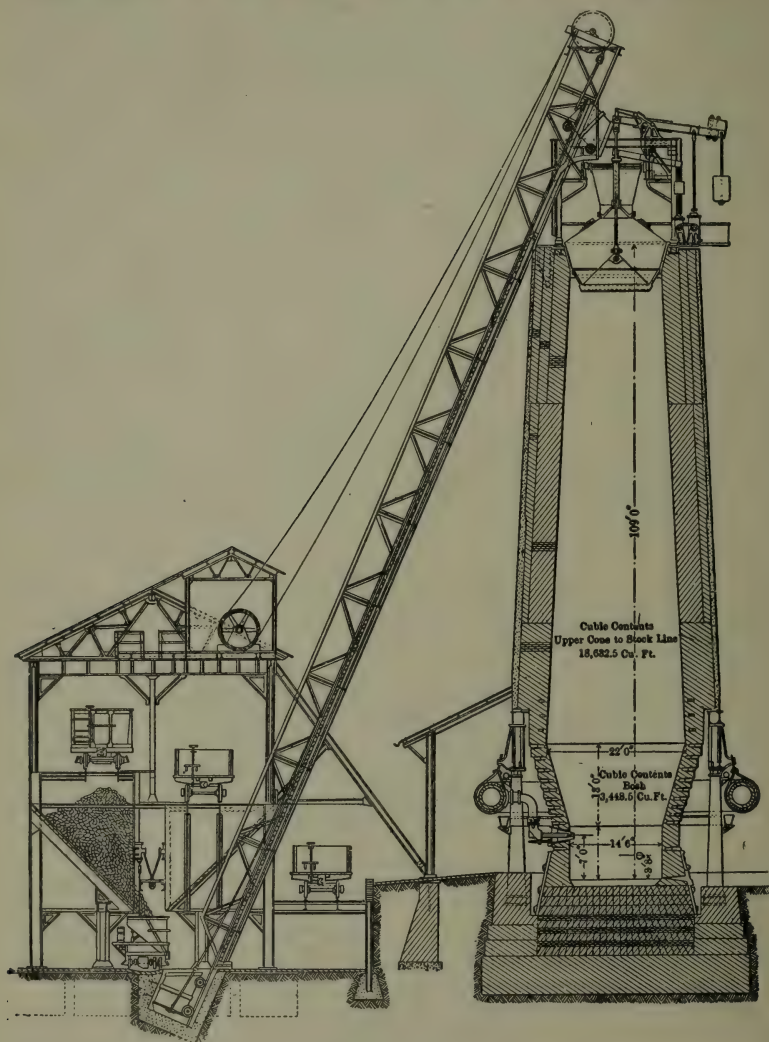


FIG. 152.

for closing the throat of the furnace and for collecting the waste gas. The *cup and cone* invented by Parry is the arrangement generally used. The throat is closed by an iron cup-shaped



casting, the diameter of which at the lower end is about one-half of that of the throat of the furnace. Beneath this cup a cast-iron cone is suspended from its apex, and when the charge has descended from the cup which forms a hopper, the cone is raised so as to completely close the throat, and the gases pass out through a lateral pipe.

In Germany, arrangements are largely used by means of which the gases are withdrawn from the centre of the throat instead of from the sides. The apparatus of Langen and of Von Hoff afford good examples. In the former, the bell-shaped tube which closes the throat is raised, whilst in the latter it is lowered in order to allow the charge to fall into the furnace. In both cases, gas-tight joints are obtained by the aid of water-troughs. A double bell is now in general use, and this is seen in position in fig. 152.

Blast-furnaces are very largely used in the smelting of lead and copper ores, and the size and capacity of these furnaces have undergone a wonderful development during the last ten years.

With a view to produce a better distribution of heat, Truran proposed, in 1857, to increase the sectional area of the blast-furnace from the hearth to the throat. This plan was adopted by Raschette in 1862. His furnace in section is a narrow rectangle with six or eight tuyères on each side, placed so as not to be directly opposite. As the blast is distributed over a large section in the zone of fusion, the combustion in this furnace is perfect, and a large out-turn is possible. It is largely used for smelting lead and copper ores. The Raschette furnace used for smelting lead ores in the Upper Hartz is 20 feet high, 7 feet 6 inches long, 4 feet 10 inches wide at top, and 3 feet at bottom. There are five tuyères at each side, and, in the more recent furnaces, one at each end.

Rectangular furnaces of the Raschette type are largely used in Colorado for lead-smelting. The furnace is formed of two independent parts, the masonry stack, *a* (figs. 153 and 154), supported on a main cast-iron plate, *b*, resting on cast-iron pillars, *c*, and the crucible upon which rest the water-jackets. These constitute one of the greatest improvements ever introduced in the construction of blast-furnaces. They are hollow boxes, made of cast iron, malleable iron, or steel boiler-plate, in which water circulates freely, so that the temperature of this portion of the furnace-wall, where the most intense heat prevails in the interior, never exceeds 70°. The water-jacket arrangement is always sectional, so as to afford every facility for the removal of the jackets when the furnaces need important repairs. This arrangement must be highly commended, as it admits of the expansion and contraction of this portion of the furnace without altering the relative positions of the parts. The im-

portance of this arrangement will be appreciated when it is

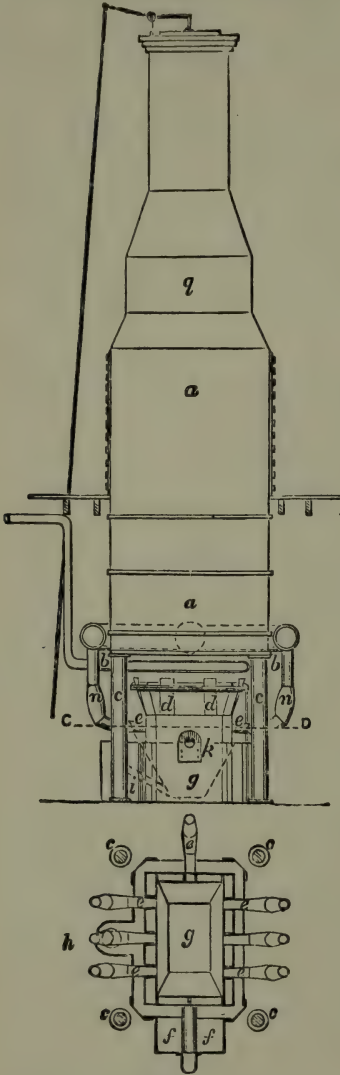


FIG. 153.

Raschette Furnace.

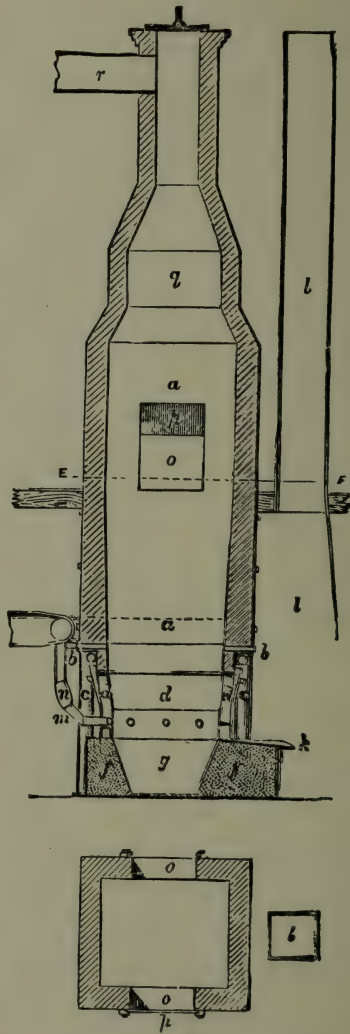


FIG. 154.

stated that smelting campaigns of thirteen months are known at Leadville.

The Leadville rectangular furnace is shown in the accompanying figures, 153 and 154, which are drawn to a scale of 9 feet to the inch. The dimensions of the furnaces vary at the different works, as the daily smelting capacity varies from 15 to 40 tons. The water-jackets, *d*, are, in the furnace represented, twelve in number, bolted together and provided with openings for the tuyères, *e*. A cold-water pipe runs round the furnace, and supplies water to the water-jackets. The lower ends of the latter rest on the hearth, *f*, which consists of cast-iron plates lined with fire-bricks or brasque. The usual form of the bottom is shown at *g*. The hearth-plates enclose the lead-well, *h*, and the channel, *i*, through which the molten lead rises to the level that it occupies in the furnace, and can be ladled into moulds without interrupting the work. At the side of the furnace, an opening is left in the water-jacket for tapping off the slag, which runs down the gutter, *k*, when the clay stopping the aperture is pierced. A hood, *l*, is placed so as to carry off any fumes evolved during tapping. Cold blast is now practically always used, and the tuyères are connected to the blast-pipes by flexible canvas hose, *n*, and a slide, *m*, at the elbow of the nozzle, admits of looking into the interior of the furnace.

The feed openings, *o*, are closed by counterpoised doors, *p*, and the furnace terminates in a short chimney, *q*, communicating by a flue, *r*, with dust-chambers.

Blast-furnaces of the Pilz type, first introduced in 1875, are also used in Colorado; but the rectangular furnace of the Raschette type is generally preferred, as it is less expensive in construction. In Europe, on the other hand, the former has almost entirely superseded the latter. The Pilz furnace, which is generally employed for smelting mixed ores of lead and copper, is circular in section. Its internal profile, which is shown in fig. 155, differs from any of the types given in fig. 151. In this case  $\frac{H}{D}$  is more than 3, but the widest part is at the top,

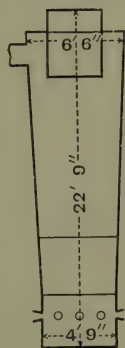


FIG. 155.

the contraction being gradual to the "crucible" portion of the furnace in which the tuyères are placed. The actual area at the throat is, however, much restricted by a cylinder of wrought iron through which the charge is introduced. The appearance of the exterior of the furnace, as used at Freiberg, is shown in fig. 156.

Prof. Gowland,<sup>1</sup> in his presidential address before the Institu-

<sup>1</sup> *Trans. Inst. Min. and Met.*, vol. xvi., 1906-7, p. 265.

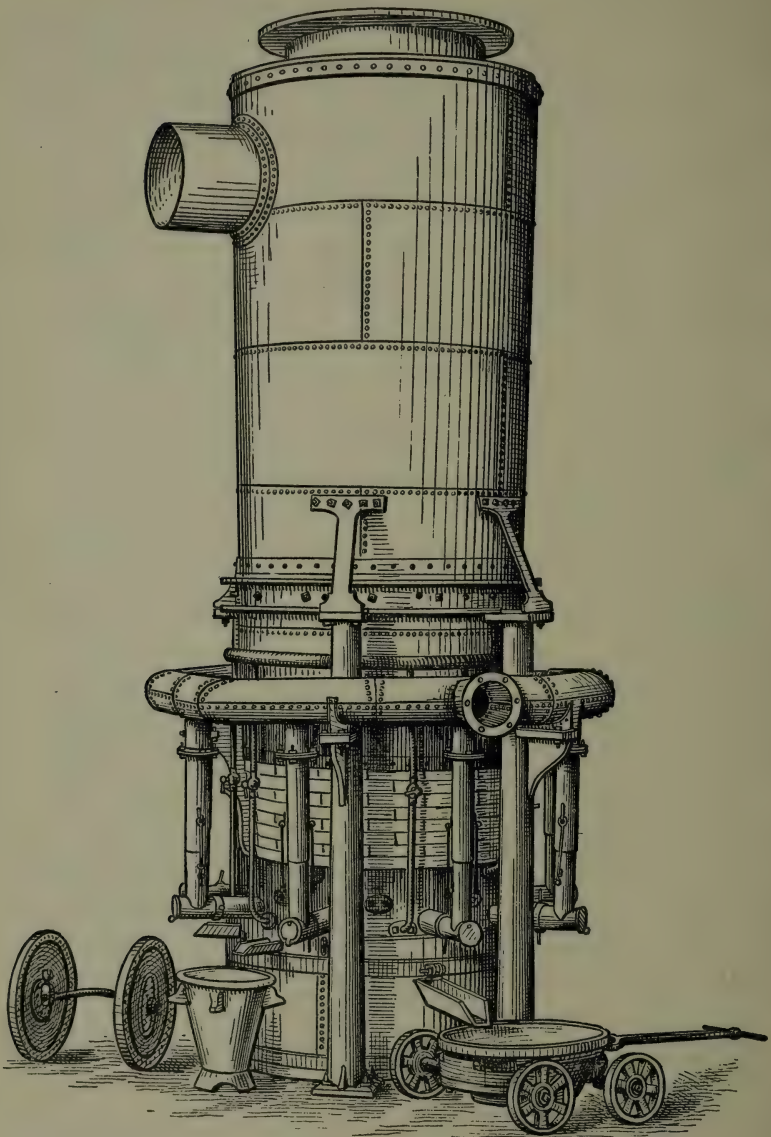


FIG. 156.—Pilz Furnace.

tion of Mining and Metallurgy, reviewed the chief advances in copper-smelting in modern times, and illustrated the gradual



development of the blast-furnace for copper-smelting during the

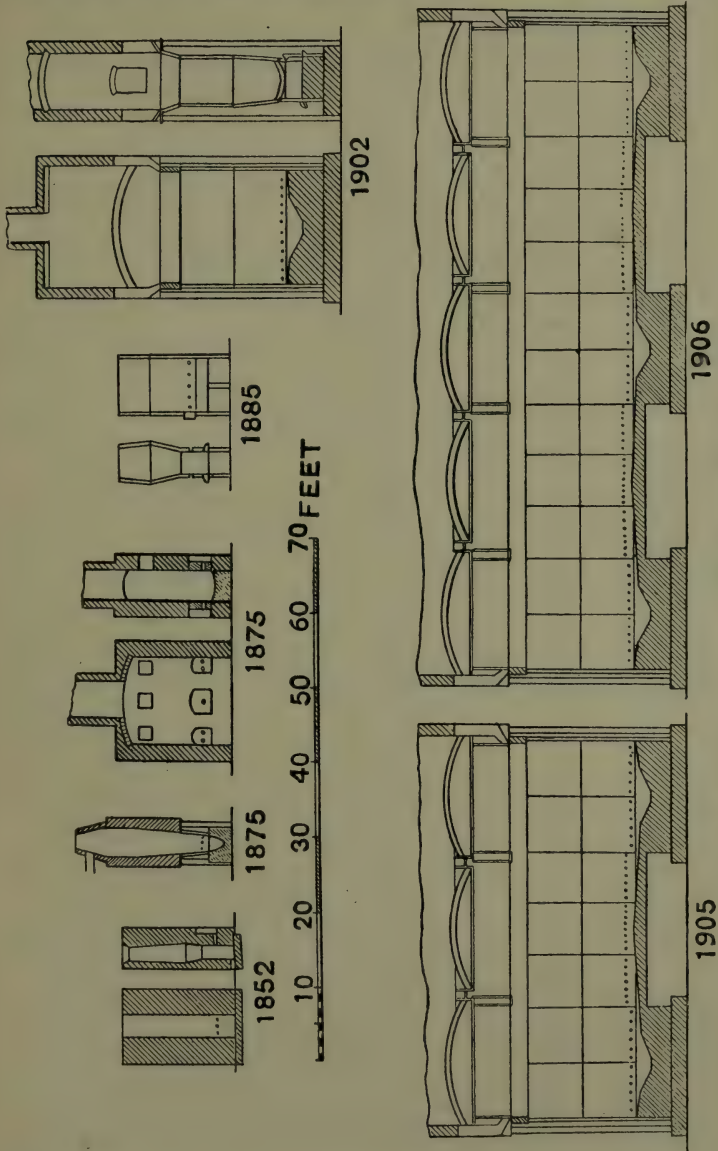


FIG. 157.—Development of the Copper-Blast Furnace.

last fifty years. Fig. 157 is taken from this address, and shows the following furnaces ;—

1852.	Mansfeld Furnace.
1875.	Pilz                    "
1875.	Orford                 "
1885.	Parrot Silver and Copper Co. Furnace.
1902.	Washoe Furnace of the Anaconda Co.
1905.	"                    "                 "
1906.	"                    "                 "

Up to the year 1885 the largest copper blast-furnaces were only of small size, being 96 inches long by 36 inches wide, and up to 1902 the largest furnaces used were 120 inches by 42 inches. In 1902, however, a complete modification of furnaces was commenced by the Anaconda Co., by building a furnace 180 inches by 56 inches. Since this date immense leaps have been made by the same company, first in 1904, by joining up two

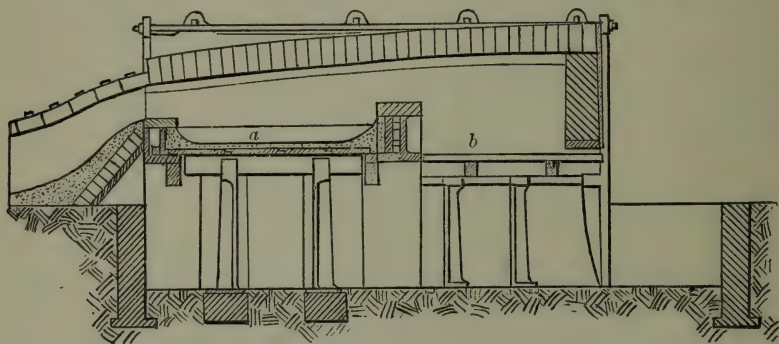


FIG. 158.—Puddling-Furnace.

adjacent furnaces, including the 21 feet space between, making a furnace of the total length of 52 feet. In 1905 another enlargement was made by joining up this 52 feet furnace to another 15 feet furnace, including a space of 21 feet, giving a furnace of the enormous length of 87 feet.

**III. Reverberatory Furnaces.**—These are constructed of very varied forms and dimensions, but their construction is guided by principles common to them all. Reference to figs. 158 and 159 will show that the reverberatory furnace consists of two main portions, the fireplace (either an ordinary grate or a producer) and the laboratory part, the fuel being separated from the ore, or the material to be heated, by means of a *fire-bridge*, which is simply a wall of refractory brick, usually furnished with an air-channel to keep it cool, and sometimes provided with orifices which admit air into the furnace. As the flames pass over this bridge and *reverberate* into the laboratory part, it will be evident that its height in relation to the position of the roof has to be

regulated with much care, for on it will depend whether the flames act directly or by radiation on the material to be heated.

The laboratory part is connected by means of a flue with a chimney, which serves for the withdrawal of the waste gases,



FIG. 159. — Roasting-Furnace.

and in many cases also for the production of draught. A damper at the base of the chimney or in the flue enables the current of air to be regulated; and, taken in connection with the thickness of the layer of fuel burnt on the fireplace, the atmosphere may be rendered oxidising, neutral, or reducing, at will. Figs. 158 and 159, exhibiting two extreme cases, show how much the dimensions

of the laboratory part in relation to the fireplace may vary. In fig. 159 a more or less pulverulent material has to be kept comparatively cool at the end of the furnace furthest from the fireplace, *b*, and to be gradually advanced to the hottest part, which is, of course, in close proximity to the fireplace. On the other hand, in fig. 158, a puddling-furnace, the material, although energetically stirred, retains its original position on the bed, *a*, and has to be actually melted. In the former case the bed of the furnace is a plane, which may slope, but which is usually horizontal. In cases similar to the latter, in which the charge has to be wholly or partially melted, the bed is concave. The nature of the material of which the furnace-bed is composed is very varied. In cases where the temperature is not high, as in the calcination of lead ore, fire-bricks, which need not be very refractory, are used. In copper-smelting furnaces some 2 feet of siliceous sand is rammed tight. Brickwork is unsuitable for this purpose, as the regulus or copper resting on it works down through the joints. In Swansea the furnace-bottoms are made of a moderately refractory sand containing 88 per cent. of silica. In certain lead-smelting furnaces the working bottom of the furnace is made of the grey slag supplied by the furnace itself. The bed of the puddling-furnace introduced by Cort was made of sand. In 1818 iron plates covered with oxides were substituted for the sand bottom with great advantage.

#### EXAMPLES OF REVERBERATORY FURNACES.

	1. German Long-bedded Calciner.	2. Copper-furnace for Regulus, Washoe Plant, Anaconda Co., 1906.	3. Cwm Avon (S. Wales), Copper-furnaces (Levy).	4. Butte Copper-furnace for Matte, 1903.	5. Flowing Lead-furnace.	6. Flintshire Lead-furnace.	7. South Staffordshire Puddling Furnace (Model in the School of Mines).	8. English Cupellation-furnace.
	ft. ins.	ft. ins.	ft. ins.	ft. ins.	ft. ins.	ft. ins.	ft. ins.	ft. ins.
Length of hearth .	39 0	116 0	16 0	50 0	11 6	11 0	5 3	1 9
Width of hearth at middle .	10 0	19 0	12 0	20 0	7 0	9 6	4 9	4 0
Length of fireplace .	6 6	7 0	4 0	5 0	2 6	2 6	3 9	2 0
Width of fireplace .	1 6	16 0	4 0	10 9	2 6	4 3	3 9	1 10
Depth of fireplace below top of bridge	...	...	3 6	...	2 6	1 9	1 6	1 9
Height of bridge above hearth .	...	...	...	...	1 0	0 9	0 6	...
	tons.		tons.	tons.		ton.		tons.
Weight of charge .	3	...	3.3	85-100	...	1	...	2



In the table on the preceding page the dimensions of typical reverberatory furnaces are given. No. 1 is a German furnace for roasting galena, a long-bedded calciner (*Fortschaufelungssofen*). There are four working doors: 15 cwt. of raw ore are charged in every six hours at the flue end of the furnace. The furnace is thus able to calcine 3 tons of ore in twenty-four hours. No. 2 is the largest reverberatory furnace in the world. It belongs to the famous Washoe plant of the Anaconda Company and is used for the production of copper matte.

No. 3 is the South Wales copper-furnace, the same dimensions applying to the furnaces for ore-smelting, for the smelting of the different kinds of regulus known as "blue metal," for white metal, and for blister copper. No. 4 is an American furnace used for ore-smelting. This is in use at the Butte Reduction Works for matting ores, the charge being 85 to 100 tons. No. 5 is the so-called flowing furnace, formerly used for lead-smelting by the Cornish method. There are two doors on each side. The charge is 2 tons of calcined ore, which is spread over the sloping bed. It melts in about three hours. The charge is then mixed with lime and anthracite, and 2 cwt. of scrap iron are placed in the furnace at the tap-hole. The charge is then remelted, and the furnace tapped by means of an iron bar. The reduced lead flows into a pot outside the furnace, and is followed by regulus formed in the reduction of lead sulphide by iron in the second fusion. Finally, the slag begins to flow, and runs along a gutter into a pit outside. The whole operation occupies eight hours, the consumption of coal being 9 cwt. per ton of ore. No. 6 is the Flintshire furnace used for lead-smelting. There are three doors on each side, the front ones being used for stirring the charge, and the back ones for tapping the slag. The roof is low, and inclines towards the flue end. In the middle there is a hopper for charging. The bed slopes from all sides towards a well in front of the tap-hole, where reduced lead collects. The usual charge is 21 cwt. of ore, the consumption of coal being 12 to 16 cwt. No. 7 (fig. 158) is a South Staffordshire puddling-furnace, which may be taken as typical of this class. There is a model of it at the School of Mines, London. The roof is a low, flat arch, with a slight slope towards the flue end. The working door, placed at one side of the furnace, is about 10 inches above the furnace-bottom. It is closed by a fire-brick slab suspended from a lever. Below the door is the tap-hole, which is closed with sand during the working of the furnace. No. 8 is the English cupellation-furnace, in which lead is separated from silver by the joint action of air and heat. The bed of this furnace is movable and is made of bone-ash, a material that resists the corroding action of the litharge (lead oxide) formed during the process. The movable bed, or *test*, consists of an oval wrought-iron frame lined with bone-ash. One end of the test is perforated with a number of

holes through which the litharge, as it forms, flows into a receptacle below. A large portion of the litharge is, however, absorbed by the bed. Air is supplied by means of a tuyère. In the German cupellation-furnace, which is also of the reverberatory type, the roof is movable and the bed fixed. The latter is concave and circular, 8 to 10 feet in diameter; it is made of marl. The roof consists of a movable iron cover lined with clay. A pair of inclined tuyères at one side of the bed supply the necessary air, and the litharge flows off through an opening on the opposite side.

The following illustration, fig. 160, showing the development of copper reverberatory furnaces, is taken from Prof. Gowland's review of advances made in copper-smelting.<sup>1</sup>

It will be seen what enormous strides have been made in increasing the size of copper-matting furnaces. It must be remembered that each increase in size of the hearth portion of the furnace has not been accompanied by a corresponding large increase of grate area, and therefore there has been an ever-decreasing consumption of fuel per ton of ore smelted at each stage of development.

With regard to the reverberatory furnaces used for the refining of copper, there have been fewer and smaller changes in the dimensions. In 1854 the furnaces employed were about 10 ft.  $\times$  7 ft., taking a charge of 10 tons. At the present time the largest furnace is probably 30 ft.  $\times$  18 ft., refining a charge of about 75 tons. The reason for this is the difficulty of keeping a very large charge at exactly the correct pitch to ensure the maximum toughness. As a matter of fact, for this reason the present practice is to use furnaces of only moderate size, rarely exceeding 18 ft.  $\times$  12 ft.

The most important reverberatory furnace in which gaseous fuel is employed is the regenerative open-hearth steel-melting furnace of Sir W. Siemens, fig. 161. Steel is produced in this furnace by three methods: (1) by the fusion of a mixture of pig-iron and scrap iron; (2) by the fusion of pig-iron with rich oxides of iron; (3) by a combination of these two processes, this being the method now almost universally employed.

The regenerative furnace of Siemens is provided with a multiple series of passages in refractory bricks piled one over the other. These passages are traversed alternately by the burnt gases which give up their heat, and by the air or gas which enters to perform the work required in the metallurgical operation. By giving the conduit sufficient length and the hot gases a slight velocity they may be made to issue almost cold, whilst the air which it is proposed to heat gradually reaches hotter and hotter regions.

The usual form of regenerative furnace resembles an ordinary

<sup>1</sup> *Trans. Inst. Min. and Met.*, xvi., 1906-7, p. 283.

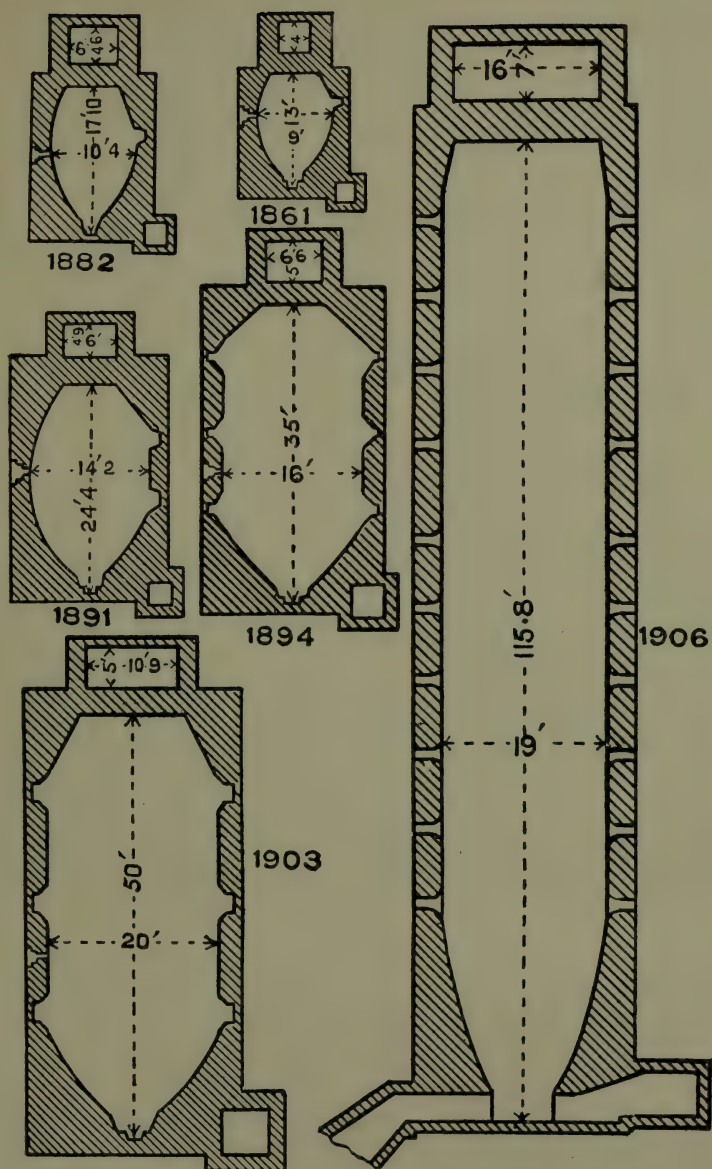


FIG. 160.—Development of the Reverberatory Furnace for Copper-Matte Smelting.



reverberatory furnace symmetrically arranged at its two ends, instead of having the grate at one end and the flue at the other. Two chambers at each end are filled with checker brickwork, space and brick alternately, so that air or gas can freely circulate. The combustible gas enters by a flue into one of these chambers, and the air to effect the combustion enters by another flue into the other chamber. The gas and air are both led to the hearth, where they meet, and the air burning the gas, the flame produced plays freely on the material on the hearth. The burnt gases

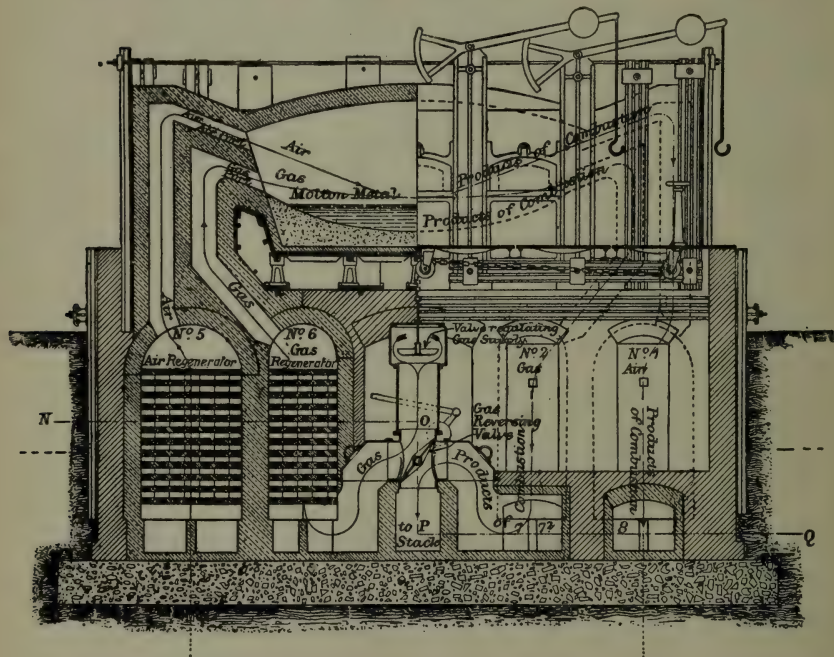


FIG. 161.

then pass into the two other chambers, at the other end of the furnace, and in slowly passing through them give up their heat to the bricks, and finally reach the chimney. In the direct flow from the gas-producer which the gases traverse there are two valves, by means of which the direction of the current may readily be reversed. When the bricks have acquired a temperature but little lower than that of the burnt gas, the valves are turned through an angle of  $90^\circ$ . The combustible gases then enter one of the chambers just heated, and the air enters the other, and in slowly ascending through the chambers they become heated at the expense of the bricks; they meet at the hearth as



before, and in burning develop a degree of heat, the intensity of which depends on the extent to which they have been heated. The products of combustion, after having done their work on the hearth of the furnace, pass through the chambers first mentioned to the chimney. When these chambers become heated, the direction of the current is again reversed, and so on.

By this alternate play of the valves the air and the combustible gas are heated; the temperature of combustion is thus increased, and a very high temperature may be obtained. At the same time, even if the temperature that would be obtained without this preliminary heating were sufficient for the required operation, it is obvious that by heating the air and combustible gas a great economy in fuel can be effected.

The great advantage of the regenerative furnace is that an oxidising, or, when only a low temperature is required, neutral, or reducing atmosphere may be obtained at will by regulating the supply of air.

The gas, it will be noted, does not come from any fireplace in the furnace itself, but is generated in a separate appliance called a gas-producer. This gas-producer consists essentially of a fire-grate on which a thick layer of fuel is maintained. The combustible part of the fuel, usually small coal, is converted very largely into carbonic oxide, hydrogen, and hydrocarbons, which are carried forward through flues to the furnaces in which they are burnt.

In the original Siemens furnace a dip-roof was used to deflect the flame on to the hearth, but in the modern furnace the roof is arched to give a larger combustion chamber, so that the gas burns out of contact with the roof or the charge. The heating of the charge is thus done almost entirely by radiation, which, apart from other advantages, has greatly increased the life of the roofs.

The tendency of late has been greatly to increase the capacity of open-hearth furnaces for steel-making. Charges of 40 to 50 and even 75 tons have become common, while furnaces holding charges of 100 to 200 tons are being used in the Talbot continuous process.

In some cases tilting furnaces are used, so that the charge can be poured instead of being tapped as in the stationary furnaces; and in the very large furnaces containing 100 tons and upwards a tilting furnace is necessary. These are of two types, known as the Campbell and the Wellman. The former is supported on rollers set in the arc of a circle, having its centre in the axis of the furnace, and the latter is supported on rockers, and tilts forward when pouring the charge. In the Campbell furnace, whatever its position, the ports are always fully open to the regenerators; but in the case of the Wellman, the ports are more or less shut off as the furnace is tilted for pouring the charge.

In order to economise labour, various forms of furnaces have been suggested: amongst these may be mentioned the Stetefeldt, in which the material is allowed to fall as a shower of dust through

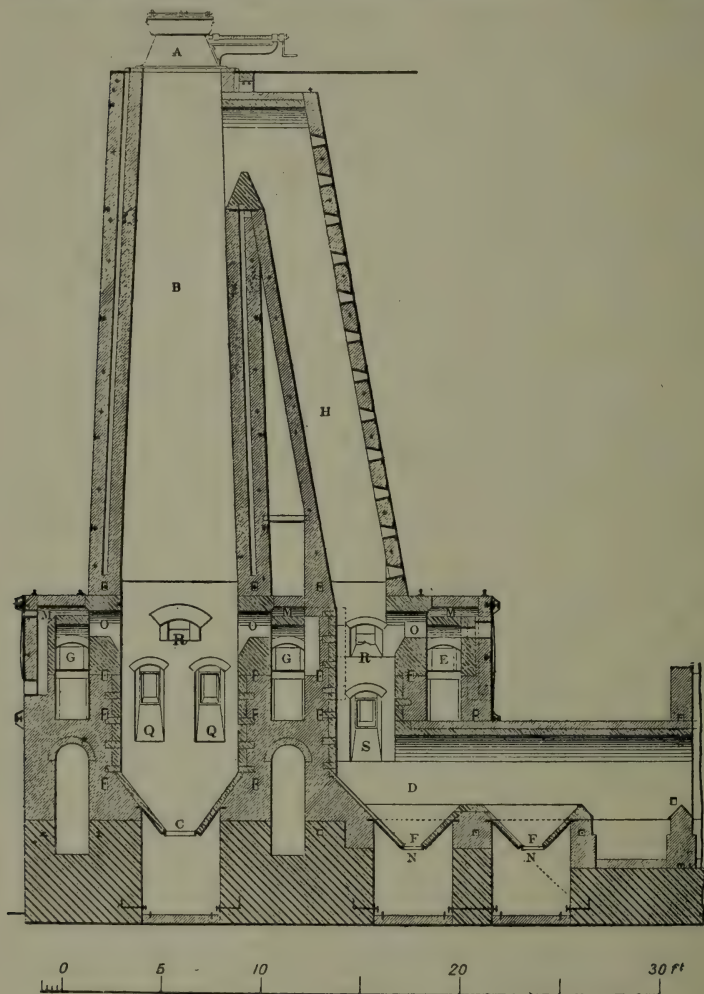


FIG. 162.

a shaft that is traversed from bottom to top by the flame from a lateral fireplace. This furnace is used for chloridising roasting of silver ores, and the pulverised ore, mixed with salt, is charged at the top of the shaft B (fig. 162) by the aid of a mechanical

feeder arranged at A on the top of the shaft. The ore falls in a slow stream down the shaft and encounters the hot gases from the gas-generators G G. For the ore which is carried along the flue H, through which the gases escape, a third gas-fire E is provided. This assists the action of the main shaft, and causes the ore to reach the flue D in a completely roasted and chloridised state, if it has not already been discharged through the hopper C. The fireplaces and arches are of fire-brick; the remainder of the furnace is of common brick. The vertical shaft is usually 30 to 45 feet in height, and 4 to 6 feet square at the base. These furnaces roast about 40 tons of ore in twenty-four hours. In Utah as much as 64 tons are treated daily. In the Stetefeldt furnace the chloridising roasting action is very rapid and complete, whilst the expenditure of labour and of fuel is small.<sup>1</sup>

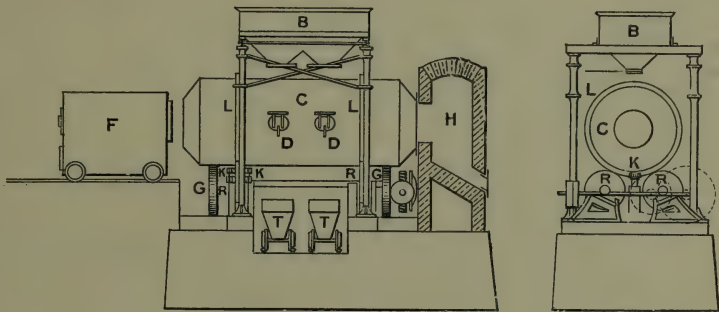


FIG. 163.—Brückner Cylinder.

The Brückner cylinder (fig. 163) is a successful modification of the reverberatory furnace, designed with a special view to the economy of labour. The roasting chamber or laboratory part of the furnace consists of a horizontal iron cylinder C, about 8 feet in diameter, which may be lined with fire-brick. The ore is introduced into this cylinder in the state of coarse powder from an ore-bin B, through two doors D D in the side of the cylinder, the latter being first rotated so as to bring the doors vertically beneath the two hoppers of the bin. The openings are closed by slides, by means of which the supply of ore to the cylinder can be controlled.

When the charge for the operation is received in the cylinder, the two doors D D are closed and bolted down, and the cylinder, which rests upon large friction rollers R R, is slowly revolved by means of the gearing G G, so that fresh surfaces of the ore are continually exposed to the action of the heated gases from a hearth F. This hearth is mounted upon wheels and stands

<sup>1</sup> *Engineering*, vol. xl., 1885, Sept. 25, p. 293.



upon a short length of rails, so that when desired it can be brought away from the end of the cylinder, and leave the latter open for examination and repair. The gaseous products pass out of the cylinder into a dust-chamber H, constructed of brickwork, and thence are discharged into suitable flues.

When the roasting is completed, the cylinder is stopped with its doors D D immediately over two trucks T T, which are placed so as to receive the hot roasted material as it is raked through the doors. Lateral movement of the cylinder is prevented by the rollers K K, which are placed so as to bear upon either side of one of the rings L L, whereby the cylinder is supported on the friction rollers. These revolving cylinders have been widely adopted for roasting copper matte and auriferous pyritic material prior to chlorination.<sup>1</sup> They differ mainly in being either continuous in their discharge (White Howell) or intermittent (Brückner).

Another form of reverberatory furnace for roasting ores and matte—the O'Hara furnace—is much used in America, and to some extent in South Wales. It resembles the ordinary roaster, but has in addition an endless chain mounted upon rollers and provided with a series of plough-shaped scrapers. The chain is kept in motion by means of suitable gearing, so that the scrapers are continually exposing fresh surfaces of ore to the action of the heated current of gases from gas-producers.

Furnaces having fixed flat beds and some form of travelling rabble form a numerous class. It may here be mentioned that the chief difficulty found is in maintaining the rabbles or rakes in an efficient condition, since these necessarily have metallic parts, and are exposed at elevated temperatures to the action of oxygen and of sulphur compounds that attack them. The more recent forms, therefore, of the furnaces of this class provide that either the rakes are continuously cooled by artificial means, or else that they are frequently withdrawn from the heated zone and allowed to cool. Pearce's Turret furnace is an example of the first-named expedient, and Brown's Horseshoe furnace of the second.

Pearce's furnace (fig. 164) consists of an annular tunnel of brickwork with a flat floor, which forms the bed in which the roasting takes place. The inner vertical wall of this tunnel is provided with a continuous horizontal slot, and in consequence of this it is necessary to suspend the inner abutment of the arched roof from a framework of girders supported from the outside. The slot is closed by a wide steel band carried by the frame on which the rabbles are suspended. At two or three points along the outside wall a fireplace is provided, with the wall itself forming a kind of fire-bridge, so that the flame from the fire can pass by a short cross flue into the bed. This flame

<sup>1</sup> Rose, *Metallurgy of Gold*.



is compelled to pass one way to the chimney by a swinging baffle-door, and, after passing round the bed, is taken from the roof by a cross flue and conducted downwards so that it traverses, but in the reverse direction, a large dust-chamber placed beneath the furnace. It is then conducted to the chimney which is outside the tunnel, and connected, as are the fireplaces, by cross flues. The ore is fed on to the bed near to the point at which the chimney is connected, and is withdrawn from the side after it has been taken successively past the fires. Its conveyance and stirring is effected by means of a series of rabblers, each mounted on a radial arm that passes through the horizontal slit already described as being in the furnace-wall. These radial arms also support the steel band by which the slit is kept closed. The arms are themselves all mounted on a central and pivoted

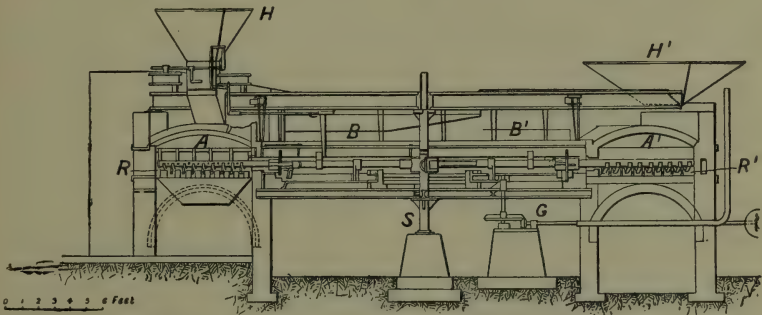


FIG. 164.—Pearce Turret Furnace. The tunnel is shown at AA' and the rabblers at R R'. These rabblers are moved from the central support S by the gearing G. Hoppers are indicated at H H'; B B' are the supporting girders of the tunnel.

pillar, which can be rotated by the usual mechanical agencies, and thus cause the rabblers to continuously traverse the roasting chamber in the direction that the ore or other material under treatment has to go, and against the current of heated air from the fires. In order that these arms and rabblers should not themselves be unduly heated, the rotating system, of which they form parts, is made with iron tubes through which the air that is required to be supplied to the bed for the roasting is continuously forced: the heating of the air which is thereby effected is itself an incidental advantage.

The Brown furnace attains the same ends as the Pearce, but by different means. There is a tunnel of brickwork, either circular in plan or formed of straight portions, joined by circular curves. This tunnel has, like the former example, a series of external fireplaces and a chimney all connected by short cross flues to it, but the chimney is more conveniently placed in the

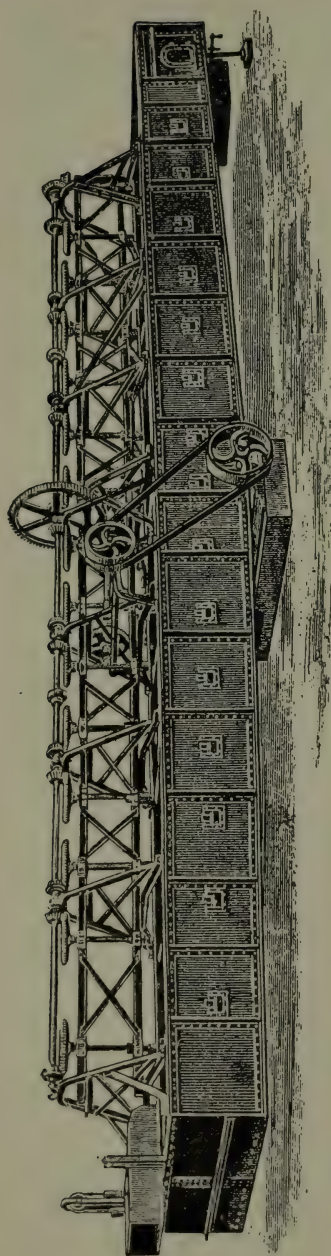


FIG. 165.—The Edwards Roaster.

centre of the circle. The tunnel, however, is not quite continuous: there being a considerable portion of the bed that does not have any roof; this necessitates the provision of two swinging doors, one at each end of the tunnel, so as to close it. The ore is mechanically fed in from above, and withdrawn through the floor after it has traversed the furnace. The rakes or rabbles are in sets, each mounted on a little carriage that is drawn through the tunnel by means of a wire rope lying and sheltered from the sulphurous fumes in a brickwork channel through which the supply of air to the furnace is made. The wire rope is prevented from coming into contact with the brickwork by means of iron pulleys, and these are placed in the air-inlets, so that, with the rope, they are kept cool and in fresh air.

The rakes will, during their passage completely round the circuit, have a period during which they pass through the open air, and are cooled before being again used. When it is desired to roast at high temperatures, this period can easily be made equal to that during which they are in the hot zone; the furnace then can be advantageously made as a straight tunnel, with the return path for the rakes behind it.

The older forms of straight mechanical furnaces were usually much shorter, and the rakes were moved to and fro

by the agency of straight iron rods, the movement being usually intermittent, so that the rakes were resting in sheltered portions of the furnace during the intervals between the successive movements.

The Edwards<sup>1</sup> calcining furnace is a single-hearthed reverberatory furnace, enclosed in a casing of boiler-plate and provided with mechanical rakes.

A general view of one type of Edwards' furnace is shown in fig. 165, a sectional view through the receiving end showing the

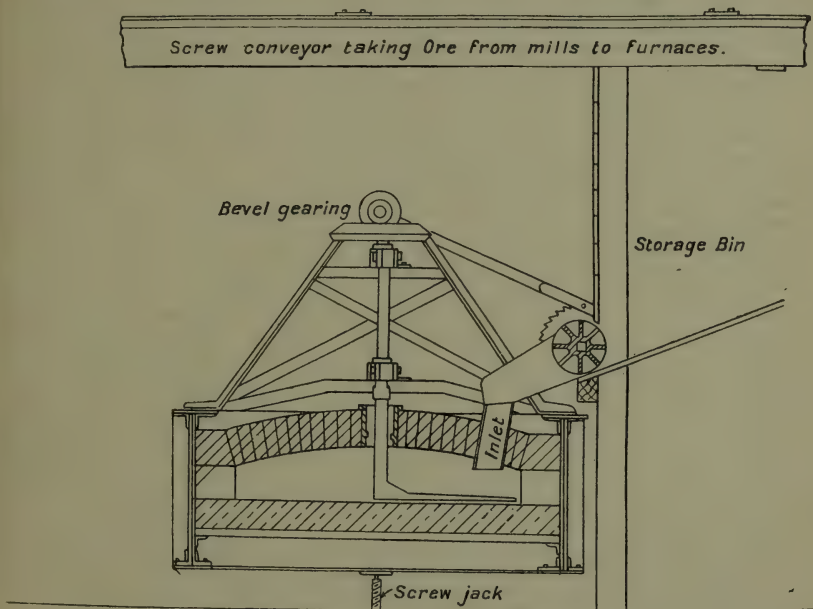


FIG. 166.—Section through Receiving End of Edwards Furnace showing Fluted Roll Feeding.

fluted roll feeder in fig. 166; and a sectional view through the discharge end, showing a water-jacketed rabble, is shown in fig. 167. The sides are made of two girders, each 60 feet long, built on the cantilever principle, and the ends of plain  $\frac{1}{4}$ -inch plate; whilst stout corrugated iron sheets, bolted to the lower webs of the girders, act as the support for the 6-feet wide bed or hearth.

The frame of the hearth, properly stayed and strengthened where necessary, is supported, about 2 feet clear of the ground, upon a couple of pivots placed midway between the ends, and it is held rigidly at the desired inclination by a couple of screw-jacks. The rabbling is done by a line of fifteen revolving rakes,

<sup>1</sup> *Trans. Inst. Min. and Met.*, xiii., 1903-4, p. 27.



with vertical stems or shafts passing through the furnace-arch; the actual stirrers are five small removable ploughs attached to a cast-iron arm which describes a horizontal circle in the ore. Each revolving rake or rabble moves in the opposite direction to its immediate neighbour, and the ore is thus made to travel in a zigzag course along the bed of the furnace.

All the mechanism is easily accessible, the rabble bearings, gear wheels, shafting, etc. being held in position in an iron framework on top of the furnace.

The five rabbles nearest to the fire-box are hollow, and are kept cool by a stream of water which is constantly passing down through a central pipe in each, and after ascending, escapes into

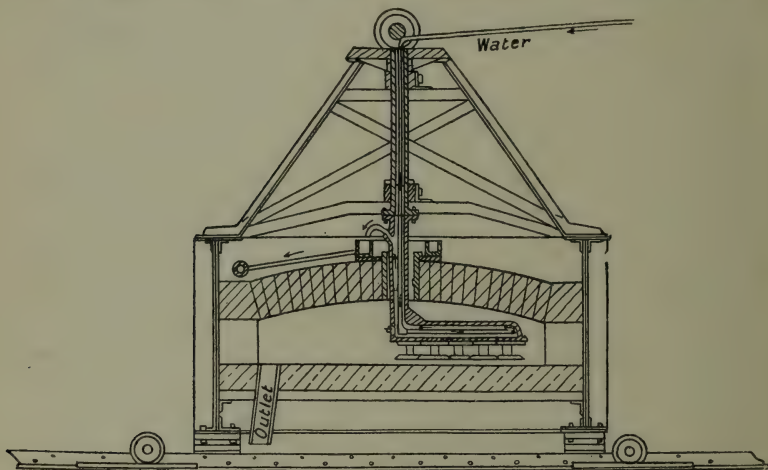


FIG. 167.—Section through Discharge End of Edwards Furnace showing Water-Cooled Rabble.

a channel ring encircling the rabble axle on top of the arch. The layer of ore is usually 2 to 3 inches deep on the hearth, and two hours are occupied in its journey from the inlet to the discharge.

Each furnace is fed by what is known as a "fluted roll," which is a cast-iron cylinder, 3 feet long and 10 inches in diameter, with eight V-shaped channels on its circumference. It is carried by a horizontal axle, to which is also keyed a ratchet-wheel with forty teeth. The roll is let into the front of the bin on a level with the bottom, and is always partly embedded in the powdered ore which fills the channels, and is discharged into the furnace as the roll rotates.

The rate of feed depends on the rate at which the roll revolves, and this is regulated by the ratchet mechanism. The power is



obtained through an adjustable eccentric, keyed on to the shaft which drives the furnace rabbles. The capacity can be altered by varying the angle of inclination of its hearth to suit the composition of the material being treated. A heavy sulphide would require a very small inclination so as to make it travel slowly towards the flame, while a partially oxidised material could be treated more rapidly by having the furnace tilted at a greater angle. This is decidedly advantageous in a customs works treating many different parcels of concentrates, etc.; but on a mine, where, as a rule, the ore does not suddenly alter in composition, the possibility of varying the inclination is of little or no use, and the tilting arrangement is left out.

The Merton<sup>1</sup> furnace, which is made in various types according to the nature of the material to be treated, has proved to be most successful, and is largely used for calcining various ores. In its main features it is somewhat similar to the Edwards calciner, but is generally built with three superimposed hearths, all perfectly level, and communicating with one another by vertical channels. The rabbles, five in number, are similar to those used in the Edwards furnace, but each rabble-stem passes through all three hearths and is supported by a footstep underneath the lowest hearth, the arms or rakes being clamped on at heights to suit the different hearths. The furnace is arranged so that the heat is gradually increased from the time the ore enters the first hearth until it leaves the third or bottom hearth, after which it passes into a finishing hearth next the fireplace, where a very high temperature is attained, which ensures the breaking up of any sulphates formed during the first part of the roast.

The M'Dougal furnace is very successful and consists of six superimposed hearths, enclosed by iron cylinders and lined with brick. It contains a vertical solid iron shaft to which are attached the six sets of arms for carrying the ploughs by means of which the ore is stirred on the different hearths.

**IV. Closed-vessel Furnaces.**—In furnaces of this class the material to be heated is separated from the fuel by an envelope in the form of a closed vessel. The vessel is heated by being in contact with the fuel, or by the flame developed from a fire on a grate, or, lastly, by the gases from a producer. The form of the vessel is determined by the process that is to be undertaken. Thus, for simple heating, the muffle is employed, whilst for fusion, crucibles are used. Retorts and similar vessels are used exclusively for distillation and sublimation.

The ordinary assay furnace may be taken as typical of the wind-furnaces used by the brassfounder. These furnaces vary according to the size and number of crucibles inserted in them. The crucible gas-furnace used for melting steel consists of a long hearth, on which the crucibles are placed in pairs. This hearth

<sup>1</sup> *Trans. Inst. Min. and Met.*, xiii., 1903-4, p. 31.

has a movable roof through which the crucibles may be withdrawn, and on the long sides are the flues from the regenerators, the construction of which is similar to that of other regenerative furnaces.

The best example of a retort-furnace is afforded by the furnace used in Belgium for smelting zinc ores. In this furnace the ores are reduced in a number of fire-clay retorts with a bellied fire-clay nozzle in which the zinc

condenses, to which a sheet-iron tube is sometimes added in which any zinc oxide is collected. The retorts are placed in rows in a vertical arched chamber with a fire-place at the base. All modern furnaces of this kind are arranged for gas firing, and fitted with regenerators similar to those used in steel-furnaces.

The furnaces are usually built in pairs, back to back. At Angleur they contain 100 retorts on either side. The charge for each retort is 66 lbs. of powdered roasted blende and 26.5 lbs. of coal.

The tube-furnace is occasionally employed in the extraction of bismuth from its ores by liquation. Native bismuth melts at  $266^{\circ}$ , and advantage is taken of this fact to separate it from the more or less infusible materials accompanying it. This process has, however, been almost entirely supplanted by ordinary smelting and wet methods. The

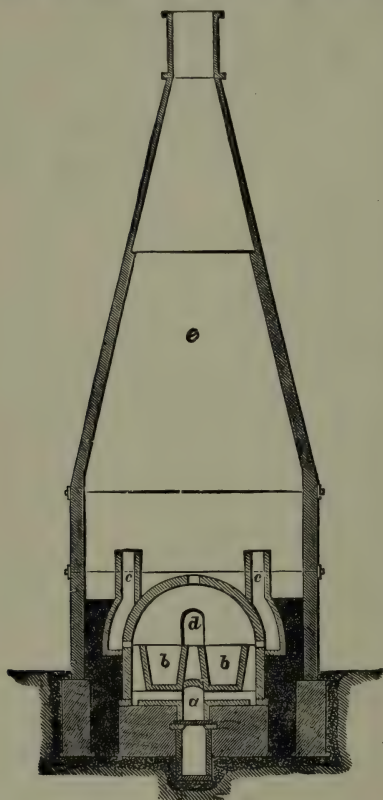


FIG. 168.—Cementation-Furnace.

liquation-furnace used at Schneeberg, in Saxony, contains a series of cast-iron tubes, oval in section, and inclining towards the front, where the ore is placed. The liquated metal is received in iron vessels heated by a separate fire.

A furnace of the closed-vessel type is used in the manufacture of steel by the addition of carbon to malleable iron, a process termed *cementation*. The furnace (fig. 168) consists of a rectangular chamber supplied with chimneys *cc*, and divided into

two parts by a fire-place *a*, on either side of which is a rectangular fire-brick vessel, or *converting-pot*, *b*, varying from 8 to 15 feet in length and 3 feet in width and depth. These pots are thoroughly heated by the flames, and the products of combustion reach the conical hood *c*, some 40 feet in height, which serves to prevent loss of heat by radiation as well as to carry off the smoke. At *d* there is a manhole, built up during the working of the furnace, but opened for cooling down and for the withdrawal of the charge.

**The Bessemer Converter.**—This furnace, fig. 169, is pear-shaped, the form originally given it by Bessemer. Unlike most smelting furnaces, the converter is usually not fixed, but supported on standards by trunnions. To one of these a pinion is keyed, by means of which the vessel can be moved through an angle of  $170^\circ$ , so that the molten metal may be poured from its mouth. The other trunnion is hollow, and admits the blast to the vessel. A pipe from this trunnion passes to the tuyère-box forming the bottom of the converter, which is perforated by ten to nineteen circular holes, into each of which is placed a conical fire-clay tuyère, perforated with twelve holes, each  $\frac{3}{8}$ -inch in diameter.

The Bessemer process was first patented on October 17, 1855, and was described in a paper read before the British Association, in which the inventor claimed a method of making wrought iron without using fuel, but it must be remembered that the combustion of the carbon, silicon, and other elements in the pig-iron during their elimination provides the heat necessary for maintaining even molten wrought iron in a fluid state. The process consists essentially in blowing large quantities of compressed air through numerous small jets into a molten mass of pig-iron, thereby effecting the rapid combustion of the carbon, silicon, and manganese present in the metal. The excitement caused by the invention in all iron-making countries was immense, as it was thought that the wrought-iron industry was doomed, since the quantity of pig-iron (about 3 tons) that a puddling-furnace could treat in twenty-four hours could be dealt with in the Bessemer converter in twenty minutes. It was, however, soon found that the expectations were not completely fulfilled; good steel could not be obtained from all kinds of pig-iron, as all the impurities could not be removed. Phosphorus, of which 1 to 2 thousandths suffice to render steel brittle and cold-short, was not removed in the ordinary Bessemer process. It was therefore necessary to employ pure pig-iron containing but a low proportion of phosphorus, until the introduction of the Basic process overcame the difficulties.

Certain modifications of the Bessemer converter have been used for many years, for example the Clapp-Griffiths, which is a small converter adapted for charges varying from 1 to 3 tons. In this

case the tuyères are horizontal, and are symmetrically arranged in the walls of the converter, near the base. The Tropenas

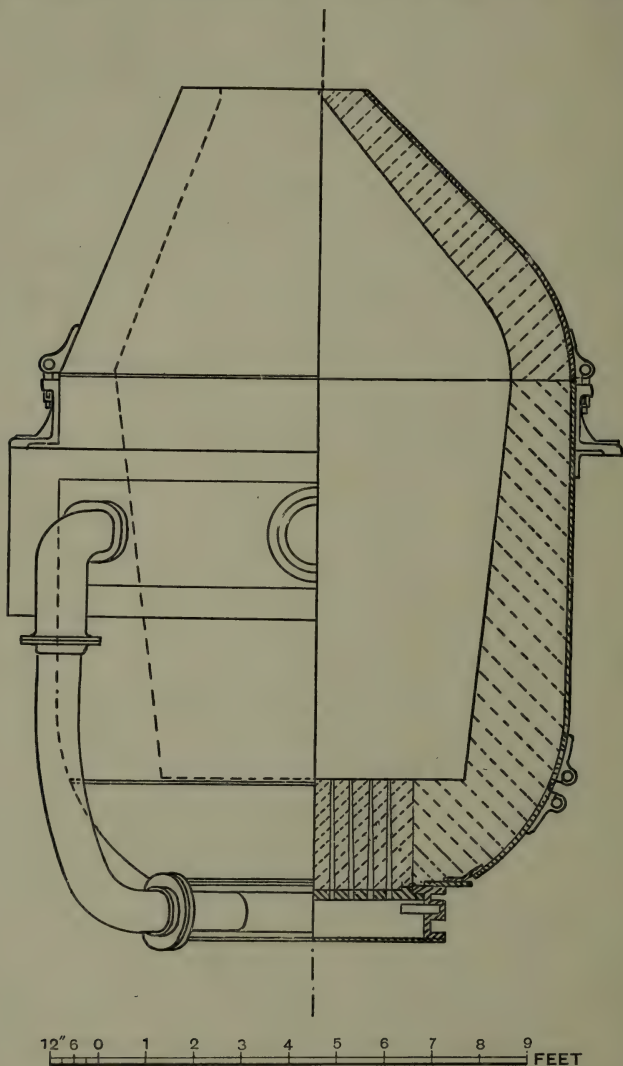


FIG. 169.—Bessemer Converter.

converter,<sup>1</sup> also a small one, is being successfully employed for

<sup>1</sup> *Mineral Industries*, vol. vii., 1899, p. 416.



manufacture of steel castings. Two blasts of air are admitted, one just above and one just below the surface of the metal, with the object of burning the carbonic oxide and so increasing the temperature of the metallic charge.

The Bessemer converter has been modified and employed for treating copper regulus. The early experiments were not successful. In 1880, however, Pierre Manhès, the proprietor of the Vedènes Copperworks, Department of Vaucluse, France, obtained patents for its use in copper-smelting, and smelting works were erected at Eguilles, near Avignon.<sup>1</sup>

More recently, the concentration of matte and its reduction to metallic copper in a Bessemer converter has received considerable attention, and many forms of modified converters have been patented.<sup>2</sup> Those in use at the present time are either vertical or horizontal cylindrical vessels. The former type resembles more closely the ordinary steel converter, except that the blast is admitted round the sides, and not through the bottom. This position of the tuyères is necessary in order to ensure that they do not come below the surface of the reduced copper, which oxidises very easily, and sets if the cold blast passes into the metal.

In 1884 the horizontal cylindrical or trough converter was designed by Manhès and David, and has since been used to a very large extent both in Europe and in America.

The earliest converters were of very small size, treating only 20 to 30 cwt. of matte for a charge. They were rotated by hand, and the operation was conducted in two stages, but gradually their dimensions were increased, and at the present time there are trough converters at Anaconda measuring 12 feet by 8 feet, and at Butte, for a special purpose, 20 feet by 8 feet, and even low-grade matte can be blown to copper in one operation.

A general view of the trough converter is shown in fig. 170.

The saving in fuel effected by the use of the converter is very considerable, and it is claimed that the Manhès process renders copper-smelting possible in countries where, owing to the high price of fuel, the Welsh process is out of the question. The Welsh process formerly consisted of six to eight successive roastings and fusions in order to obtain coarse copper from the ore, all the operations being effected in large reverberatory furnaces. In the Manhès process, by blowing air through the copper matte produced in the first smelting operation, metallic copper may be obtained ready for the refinery.

**V. Electric Furnaces.**—The electric furnace, originally devised by Sir W. Siemens, has become a powerful instrument of research, and of considerable importance in commerce.

By the aid of a small electric furnace, and using a current varying from 25 to 450 amperes, with a difference of potential

<sup>1</sup> *Annales des Mines*, 8th Series, vol. iii., 1883, p. 429.

<sup>2</sup> Peters, *Copper Smelting*, 1895, pp. 528-575.

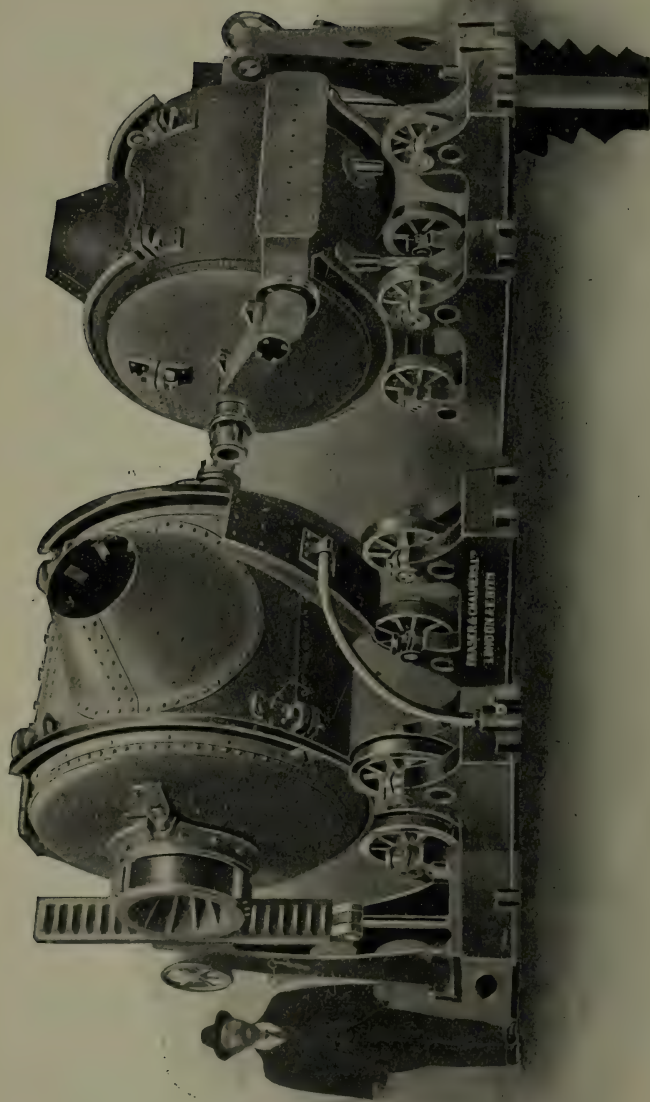


FIG. 170.—3-ton Bisbee Converter for the Treatment of Copper Matte.

at the terminals of the furnace of from 45 to 70 volts, Moissan<sup>1</sup> succeeded in fusing such refractory substances as lime, and in readily preparing samples of the difficultly reducible metals, such as zirconium, chromium, calcium. He also<sup>2</sup> made the furnace reverberatory by placing the material to be treated in a hollow tube of pure carbon placed at right angles to the electrodes. The heating and electrolytic effects of the arc are thus kept distinct. The arc may be deflected on to the material to be heated by means of a suitably disposed magnet. The work of Moissan with the electric furnace has since been published in book form.<sup>3</sup>

Electric smelting-furnaces employed in metallurgical operations may conveniently be divided into three main types:<sup>4</sup>—

- (1) Induction-furnaces.
- (2) Resistance-furnaces.
- (3) Arc-furnaces.

The first type is especially adapted for melting as distinct from smelting—that is to say, for melting down mixtures of different metals to form certain definite alloys, rather than for the reduction of the metals from their ores; the second type can be used either as a melting or smelting furnace by varying the construction, and the third type can also be adapted to either purpose. In all cases, whatever the type of furnace employed, the object is to supply the heat necessary for the particular operation by means of electric energy; in this way the electric energy simply replaces the coal, coke, or gas used for heating, and it will readily be realised that in countries where fuel is cheap, as it is in England, the circumstances are comparatively few where it can be commercially employed.

The furnaces in which an electrolytic action takes place in addition to the heating effect produced by the current may be considered as modifications of the resistance-furnaces.

For certain purposes, however, where it is important to obtain a finished product of great purity, where intense local heat and a non-oxidising atmosphere are required, electric energy enables us to meet the conditions more economically than can be done in any other way.

The induction-furnace is a large crucible in which the steel or other metal is melted by an induced current out of contact with any electrodes, completely protected from the action of any furnace gases, and practically protected from oxidation. It gives, from a metallurgical point of view, by far the nearest approach to the conditions of the crucible. The best-known furnace of

<sup>1</sup> *Comptes Rendus*, vol. cxv. (1892), p. 1031.

<sup>2</sup> *Ibid.*, vol. cxvii. (1893), p. 679.

<sup>3</sup> *Le Four Electrique*, Paris, 1897; English translation, 1904.

<sup>4</sup> See Harbord on Recent Developments in Electric Smelting in Connection with Iron and Steel, *Transactions Faraday Soc.*, vol. i., 1905; also paper, West of Scotland, *Iron and Steel Inst. Journ.*, 1909.



this type is the Kjellin furnace, which has been in operation at Gysinge, Sweden, for steel-making since 1900. Figs. 171 and 172, taken from the Canadian Commission Report, are a plan and sectional elevation of this furnace. This furnace is in effect a step-down transformer, in which the contents in the hearth or crucible form the secondary circuit of the transformer. The furnace is of 225 H.P. capacity, and to the primary, A A, fig. 171, is delivered an alternating current of 90 amperes and 3000 volts, which induces a current in the secondary, B B, of 3000 amperes and 7 volts. The primary, A A, consists of an insulated copper wire wound round one leg of the laminated core, C C C C, which forms the magnetic circuit. When an alternating current is passed through the coil it excites a magnetic flux in the core, and the intensity of the current induced in the steel is then almost the same as the primary current multiplied by the turns of the wire in the primary coil. The tension of the current is naturally reduced in almost the same ratio as the intensity is increased. In this way it is possible to use an alternating-current generator of high tension, and to obtain a current of low voltage and great intensity in the furnace.

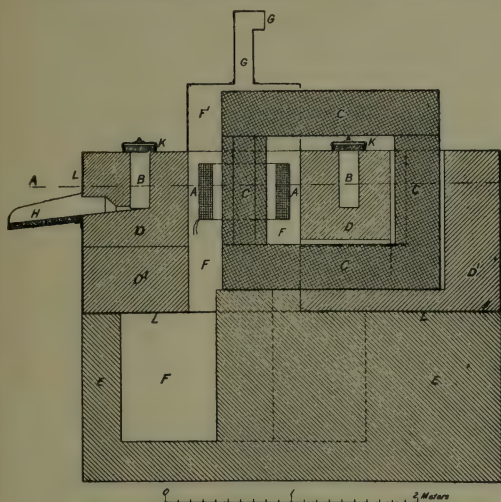
In starting the furnace, a little molten pig-iron is poured into the circular trough, B, to form the secondary circuit, and at the finish of each heat sufficient molten steel is left in the furnace to maintain this circuit. The circular hearth or crucible has movable covers on the top, of a size which can be easily raised by means of a bar, and the materials are charged in at the top by removing these covers. The charge at Gysinge usually consisted of best Swedish pig-iron, Walloon iron, and steel scrap, and the proportions of pig-iron and steel scrap are varied according to the grade of steel it is desired to produce. Any grade of steel can be produced in this furnace from 0.10 to 1.50 per cent. or more of carbon, the only thing necessary being to have ample power to ensure rapid melting, and to obtain a sufficiently high temperature to enable the steel to be cast into ingot moulds.

The Röchling-Rodenhauser furnace is a modification of the Kjellin furnace, and may be regarded as a combination of an induction- and resistance-furnace. In it certain difficulties met with in the Kjellin type of furnace have been largely overcome. In its latest form it is operated by a three-phase instead of a single-phase current, which enables a 15-ton furnace to be operated with a frequency of 50 periods instead of 25, and standard generators to be used instead of specially constructed expensive generators. A special feature of this furnace is the rotation of the charge, due to the presence of a rotary field, which ensures an automatic circulation in the bath. The charging-door is at one end of the furnace, the tapping-hole at the other, and the whole is built as a tilting-furnace.

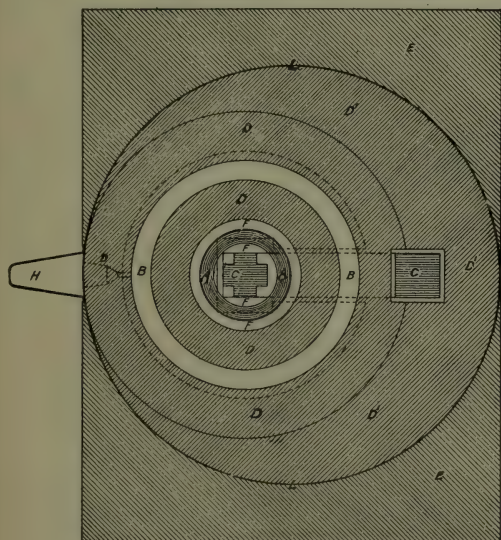
In the resistance-furnace the heat is generated by the resistance



offered by the whole or a portion of the furnace-charge to a very powerful electric current. It is best represented by the Hérault



FIGS. 171 and 172.—Kjellin Furnace. Vertical section through the tap-hole and sectional plan on A B.—A A, primary coil of insulated copper wire wound round laminated core, C, and to which is delivered an alternating current of 90 amperes at 3000 volts; B B, annular crucible or hearth, in which charge is melted and forms the secondary; C C, laminated core; D' D', fire-brick; D D, silica or magnesite brick; E E, ordinary brick foundation; F F, air-space for cooling primary; F' and G, iron cylinder with pipe attached to maintain a current of air flowing round primary; H, spout from tap-hole; K K, covers for annular crucible; L L, cylindrical iron casing of furnace. The covers of the crucible are on a level with the working-floor, and the furnace is charged by removing these and throwing the scrap and iron into the crucible, B.



Section A B

and Keller furnaces, both of which are employed commercially in the manufacture of steel and alloys of iron.

The Hérault furnace for the manufacture of steel has been in successful operation now for several years. The furnace shown

in fig. 173, taken from the Canadian Commission Report, is a tilting-furnace, so far as the construction of the body of the

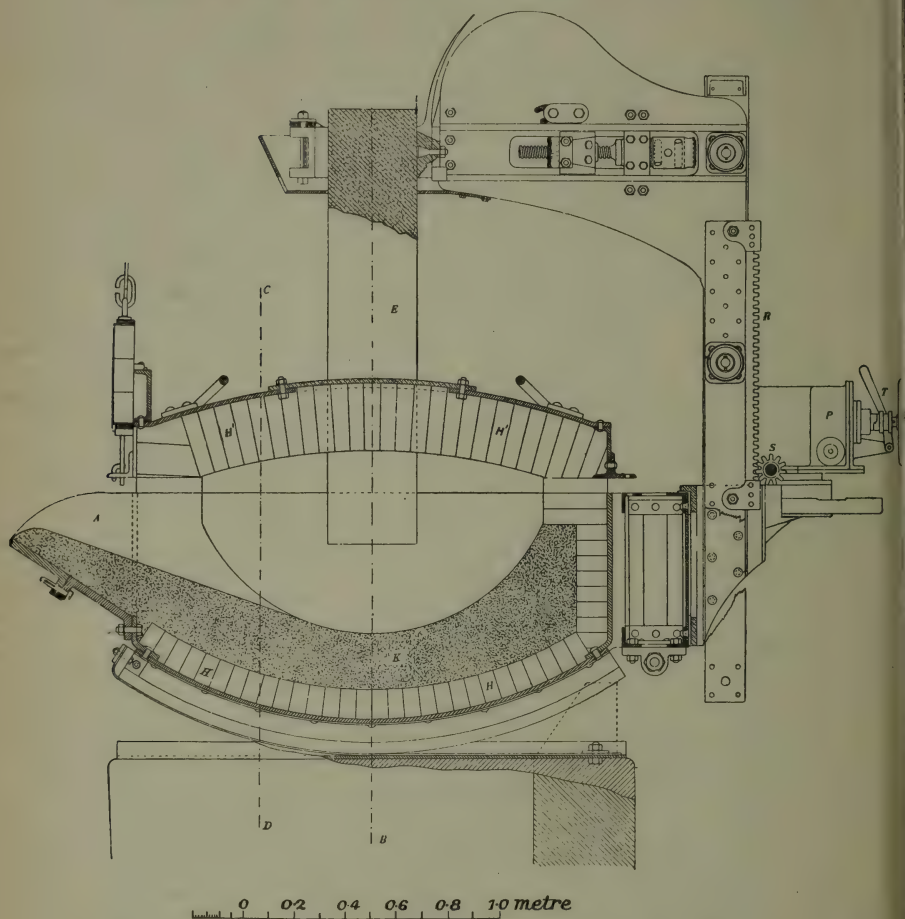


FIG. 173.—Hérault Furnace. Vertical section through the pouring spout.—A, pouring spout; E, suspended electrode, of which there are two, passing through roof; H, basic or burnt Dolomite bricks; H', silica bricks of roof; K, rammed basic material; P, motor for driving automatic regulator; T, lever for throwing motor, P, out of action; Z, hand-wheel operating pinion, S', for regulating electrodes by hand; R, rack gearing with S, by which electrode is raised or lowered. An alternating current of 4000 amperes and 110 volts is used.

furnace is concerned, very similar to that of the well-known Wellman and Campbell tilting-furnaces. The furnace-hearth is

basic-lined, as in the ordinary basic open-hearth process, and two large electrodes pass vertically through the roof, and can be raised or lowered either by hand or automatically by a specially constructed regulator. An alternating current of 4000 amperes and 110 volts is used at La Praz, and the intensity of the current passing through the bath is regulated by increasing or decreasing the width of the air-gap between the electrodes and the slag-line.

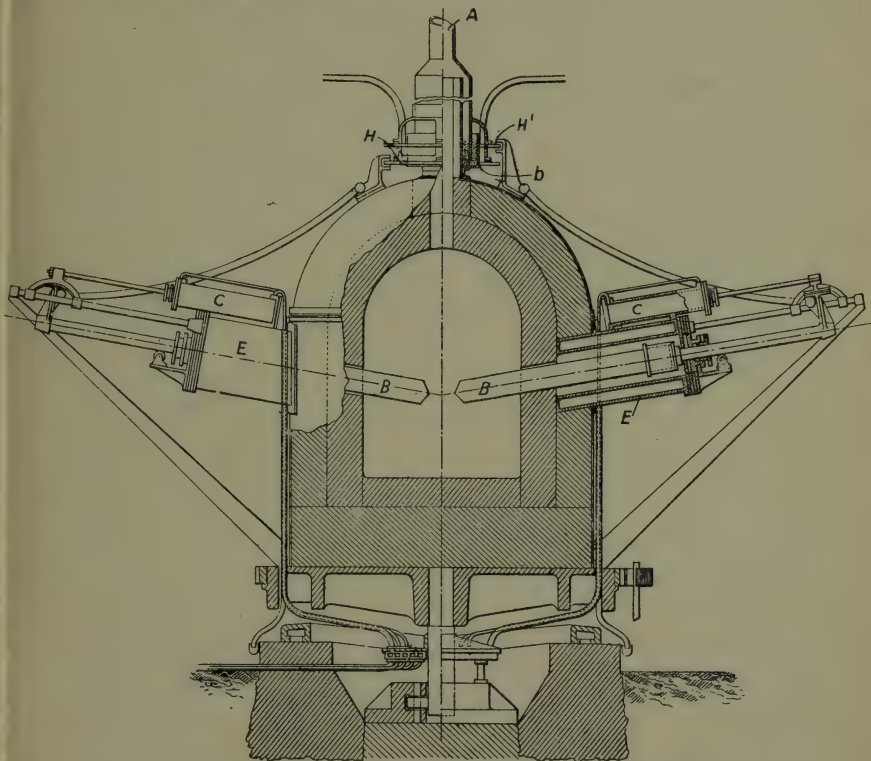


FIG. 174.—Stassano Electric Furnace. A, tube to lead off volatile products; BB, electrodes; CC, hydraulic cylinders for regulating electrodes; EE, water-jackets for electrodes.

The section of the roof between the electrodes is usually made of bronze, in order that no magnetic circuit may surround them. The electrodes may or may not be water-jacketed where they pass through the roof, but water-cooling not only increases the life of the furnace and electrodes, but enables a considerably larger output to be obtained.

In the Arc furnace the necessary heat is obtained by direct radiation from the arc and by reflection from the roof and sides

of the furnace. As far back as 1879 the late Sir William Siemens designed a small crucible-furnace capable of melting a few pounds of steel on this principle, and the Stassano furnace is the best-known furnace of this type used for the smelting of iron and steel. It is shown in fig. 174. The furnace rotates round an axis inclined about  $7^{\circ}$  to the vertical. There are three electrodes, which nearly meet in the centre of the furnace, their distance being regulated by a hydraulic ram. A three-phase alternating current is used, and distributed between the three electrodes. The Stassano furnace is rotated by mechanism underneath the furnace during the operation of smelting, but this is not essential to this type of furnace. The furnace is lined with magnesia bricks, and there is provided a tap-hole for metal at the bottom of the furnace and a slag-hole at a somewhat higher level. The charge is fed through a hopper and inclined shoot to deliver below the electrodes. Furnaces of this type are now used commercially in the production of zinc, the volatilised metal being condensed in suitable chambers.

Electric furnaces are now receiving a large amount of attention, and there is no doubt that great advances will be made in this direction in the near future.



## CHAPTER X.

### THE SUPPLY OF AIR TO FURNACES.

**Methods of producing Draught.**—In every furnace it is necessary to conduct away the gaseous products of combustion to enable fresh air to enter and to give up its oxygen to the fuel. This passage of the fire-gases from the furnace and of the air to the furnace may be effected in two ways: first, by exhausting the products of combustion; and second, by forcing in air for combustion. In the former method a space containing rarefied air is formed in the furnace, and atmospheric air flows in from outside so as to preserve the equilibrium; whilst in the latter method the pressure in the furnace is greater than that of the air outside, and consequently the air and the fire-gases are forced out. Although the current is usually the same in both cases, the influence on the combustion may be different when the movement is effected by the compression or rarefaction of the air.

The exhaustion of the air is usually effected by means of chimneys. The chimney or stack may be regarded as a vertical pipe containing heated and expanded gaseous products of combustion. The column of gas within the chimney is, in consequence of the expansion due to heat, considerably lighter than a column of air of the same height at the ordinary temperature. The consequence is that, owing to the difference of weight, there is an excess of pressure of air under the grate, and movement ensues. This difference in the weight of the hot and cold columns is equal to the weight of the increase in volume that would be produced by heating the cold column of air to the temperature of the chimney. If the elongation thus produced be represented by  $h$ , the velocity of the movement  $v = \sqrt{2gh}$ ; but  $h$  is dependent both on the height of the cold column of air and on the difference of temperature within and outside the chimney, whence it follows that theoretically the velocity of a current of gas within a chimney increases proportionately with the square root of the height and the square root of the difference of the

external and internal temperatures, and that consequently the action of equal increments of height and temperature becomes continually smaller. But the action of a chimney does not depend so much on the velocity produced as on the weight of air supplied in a given period of time. The higher the products of combustion are heated, when they pass into the chimney the greater is their volume, and, with equal velocity, the less weight of gas would actually pass through the same chimney. The velocities, it has been shown, increase with the difference of the external and internal temperatures, but only in proportion to the square roots, whilst the relative weight of the gases decrease in direct proportion to the temperature by  $\frac{1}{273}$  of the original volume for every degree Centigrade. There must therefore be a limit where the action of the chimney reaches its maximum, and it has been calculated that this maximum is attained when the difference of temperature amounts to  $273^{\circ}$ , or, in other words, when the external air is at the mean temperature and the chimney gases have a temperature of  $300^{\circ}$ . Similarly, it has been calculated that the quantities of air supplied to the chimney between  $200^{\circ}$  and  $400^{\circ}$  differ but slightly, so that for the chimney-draught these temperatures appear to be the most suitable, whilst for the utilisation of heat in the furnace the lower chimney temperature is obviously to be preferred; and even when the temperature of the chimney gases is only  $100^{\circ}$ , the quantity of air drawn in is to that drawn in by a chimney having a temperature of  $300^{\circ}$  as 7 : 8.

The amount of gas passing out of the chimney could be determined from the height and temperature of the shaft and the specific gravity of the gases if only the resistance given by friction to the gases in motion and the so-called "free section" were known. The term "free section" is applied to the sum of the areas of the interstices between the lumps of fuel on the grate. The smaller this free section is, the quicker is the motion of the air in it, and the more perfect the combustion, provided that the reduction in section is due to a diminution of the area of the grate, and not to undue clogging of the layers of fuel which, by increasing the friction, at once diminishes the action of the shaft, as the volume of air supplied is necessarily lessened. For this reason small grates give rapid combustion and large grates slow combustion with the same chimney. It has, however, previously been shown that a rapid motion of the air, in this case equivalent to rapid combustion, facilitates the production of carbonic anhydride, whilst a slow motion facilitates the production of carbonic oxide. As a rule, therefore, for the production of heat and for high temperature, rapid combustion on a small grate is to be preferred to slow combustion on a large grate.

The height of the stack must increase with (1) the rapidity of the combustion; (2) the height of the layer of fuel on the grate;

and (3) the resistance to which the current is exposed in passing from the grate to the foot of the stack. On the other hand, the height of the stack must increase in inverse ratio to the temperature of the evolved gas.

For furnaces in which the combustion is not rapid, and in which there is but slight frictional resistance, as in furnaces from which the gases pass directly to the shaft, the height of the stack need not exceed 33 feet. Welding-, puddling-, and other furnaces in which the combustion is rapid require a shaft at least 50 feet in height if the gases pass into it at a high temperature; but if they are cooled on their way, and have great frictional resistance to overcome by being utilised, before they reach the shaft, for other purposes, as for heating steam-boilers, it is advisable to make the shaft 65 to 80 feet, or even 100 feet if the length of the flues is considerable, and if they are narrow and crooked.

A chimney is frequently arranged so as to be common to several furnaces, and in this the gases from all the furnaces unite. Its section is calculated on the assumption that the minimum velocity of the gases in the chimney ( $6\frac{1}{2}$  feet per second) is not exceeded, even if only one of the furnaces be working and the others are cold. At the same time, in order to prevent an unduly decreased velocity when all the furnaces are at work, the common shaft must be made of considerable height, usually 130 to 165 feet. To ensure the successful working of chimneys of this kind, it is important that the up-currents should pass into the shaft in parallel directions, so as to prevent suction being arrested by the impact on each other by converging streams of gases. In order that cold air shall not be drawn into the shaft from a furnace that is not being worked, every flue passing from the furnaces to the shaft must be furnished with a damper.

The vertical projection of the interior of the shaft may be either of the same width above or below, or there may be a slight narrowing at the top. The tapering shape increases the stability of the shafts, especially when they are exposed to the action of storms. It has been proved theoretically that a slight divergence towards the top gives a better draught. The angle at which the sides are inclined to the perpendicular should be 0.5 to 1.5 degree.

Any cooling of the gases interferes with the draught. For this reason brick shafts are preferable to iron ones, and the interior should be made as smooth as may be, so as to lessen friction.

The first researches on chimney gases are due to Péclet, who published some analyses in 1828; but his results, and those of different experimenters who followed him, were open to the objection that the samples taken for analysis were only small fractions of the total gases in the flues, and, as they were not taken with sufficient frequency, they could not represent the



mean composition. This grave defect was, however, remedied by Scheurer-Kestner in an elaborate research on the composition of the flue gases of boiler furnaces, which will always form the basis of future experiments in this direction.

A series of experiments conducted by this distinguished chemist and Meunier, in 1868, on the combustion of fuel in boiler-furnaces, showed the difficulty of burning fuel completely on the grate of a furnace; and the analyses of the gases made by them led to the conclusion that the products of combustion always contain unburned constituents, even in the case of a thin layer of fuel and an excess of air of more than 50 per cent.; that is to say, with volumes of 240 cubic feet of air for every pound of coal burnt, instead of 128 to 160 cubic feet. They also showed that the mean proportion of unburned hydrogen reached 20 per cent. of the total amount present. This points to the fact that hydrogen is more difficult to burn, even under favourable conditions, than carbonic oxide, and that with a thin layer of incandescent fuel the unburned carbon in the gas exists more often in the form of a hydrocarbon than in that of carbonic oxide.

In securing a representative sample of gas, the position of the flue from which the gases are withdrawn is by no means a matter of indifference. With a view to collect soot, it should, of course, be as near to the incandescent fuel as possible; but Cailletet has shown that the gaseous products from furnaces must not be collected immediately after being liberated from the fuel, for a current of gases from a mass of incandescent fuel may contain notably more carbonic oxide than the same gases do when cold—that is, during the cooling, combination of carbonic oxide and oxygen takes place.

In a series of tests made by the author<sup>1</sup> in connection with an exhibition opened with a view to abate the nuisance arising from smoke, 85 cases showed that the relation by weight between the carbon completely burnt to carbonic anhydride and that present in the form of hydrocarbons or carbonic oxide varies between the limits of 1000 : 4 and 1000 : 375. There were, however, only 9 cases in which a ratio of 1000 : 200 was exceeded, and but 3 in which the ratio was less than 1000 : 10.

In 17 cases given by Scheurer-Kestner this relation varied from 1000 : 10 to 1000 : 211, the result being mainly dependent on the amount of air introduced to effect the combustion. With reference to the hydrogen, it is to be observed that in these experiments the proportion of carbon completely burnt to carbonic anhydride to the hydrogen present, either in the free state or as hydrocarbons, varies from 1000 : 3 to 1000 : 16. The loss of carbon in the form of soot never exceeds 1 per cent. of

<sup>1</sup> *Report of Smoke Abatement Committee*, London, 1882, in which volume there are references to the literature of the subject.



the fuel burnt, while the mean loss is probably between 0.5 and 0.75 per cent.<sup>1</sup>

In many cases it is important to be able to keep a record, and so be able to control the composition of waste gases; and within recent years a number of forms of apparatus have been devised for the automatic analysis of furnace gases, based upon the determination of the contained carbon dioxide.

The methods adopted may be divided into two classes—those depending on the specific gravity of the gases, and those in which the carbon dioxide is removed by absorption. The former include the Lux gas-balance,<sup>2</sup> Arndt's Oekonometer,<sup>3</sup> and similar apparatus devised by Pfeiffer,<sup>4</sup> Siegert, and Krell.<sup>5</sup> Since the specific gravity of the furnace gases is not only dependent upon the proportion of carbon dioxide present, but also upon that of the contained water vapour and unburnt gases, and is, moreover, variable with the pressure, results based upon this method of examination can only be regarded as approximate, and are not sufficiently accurate or reliable to substitute the ordinary analytical methods. The forms of apparatus in which the carbon dioxide is absorbed are more reliable, as their method of working is based upon the removal of the specific constituent, the percentage of which is required to be known. The forms of apparatus based on this principle include the "Ados" or "Sarco" apparatus,<sup>6</sup> the Simmance-Abady "Combustion Recorder,"<sup>7</sup> the apparatus of C. Jung,<sup>8</sup> that of H. J. Westover,<sup>9</sup> that of W. H. Porter,<sup>10</sup> the Uehling-Steinhardt "Gas Composimeter,"<sup>11</sup> and the Autolysator<sup>12</sup> of Stracho Johoda and Genzken.

Of these, the Ados and Simmance-Abady Combustion Recorder are the best known in this country. Both depend upon the absorption of the carbon dioxide by means of a solution of potassium hydroxide and the subsequent recording of the decrease in volume effected by the absorption, whereby an intermittent estimation of the carbon dioxide in the furnace gases is effected at successive short intervals.

**Blowing-Engines.**—The mechanical appliances employed for the production of a stream of compressed air are so varied in

<sup>1</sup> For fuller information on this subject the student is referred to Gruner's *Traité de Métallurgie* and Ledebur's *Die Oefen*.

<sup>2</sup> Lux and Precht, Fischer's *Jahresber.*, 1893, xxxix. 1205.

<sup>3</sup> *D. R. P.*, 70,829, 125,470, 129,163.

<sup>4</sup> *D. R. P.*, 78,612.

<sup>5</sup> *Verein deuts. Ing.*, 1888, xxxii. 1090; 1893, xxxvii. 595.

<sup>6</sup> *Ger. Pat.*, 160,288. *Zeit. angew. Chem.*, 1905, xviii. 1231.

<sup>7</sup> *Eng. Pat.*, 18,680, 1906.

<sup>8</sup> *Chem. Zeit.*, 1905, xxix. 445.

<sup>9</sup> *U.S. Pat.*, 833,274, 1906.

<sup>10</sup> *Eng. Pat.*, 9540, 1906.

<sup>11</sup> *Eng. and Min. Journ.*, vol. vii. p. 608.

<sup>12</sup> *Zeit. Chem. Apparatenkunde*, 1907, ii. 57; *Journ. Soc. Chem. Ind.*, 1908, xxvii. 608.

their details that it is impossible to do more than allude to them, the construction and the principles involved falling more in the province of the mechanical engineer than in that of the metallurgist.

In early times the blast was obtained solely from leathern bellows, which were at first single-acting, and subsequently double-acting, but as leather soon becomes inflexible and brittle, it was found advisable to employ wooden bellows. In this way was evolved the box-blower, with single-acting movement of a piston. In the course of time cast iron was substituted for wood, and the iron blast-cylinder, one of the forms of blowing-engines still in general use, was obtained. In addition to this, for low pressures and large volumes of blast, fans and blowers are largely used.

A blowing-cylinder consists of a cast-iron cylinder fitted with a piston receiving a reciprocating motion from the crank-shaft of the engine. At every stroke, air is drawn into the cylinder on one side, and on the other compressed air is forced into a reservoir or into the blast-main. The interior of the cylinder is connected with the atmosphere on the one hand, and with the blast-main or reservoir on the other, by means of flap- or disc-valves fitted in the cylinder-covers. The piston is actuated by engines of the vertical direct-acting or of the beam-engine type, the former being now generally preferred. On the Continent the blowing-engines are frequently of the horizontal, direct-acting, condensing or compound class. The amount of blast required to be delivered is often very considerable, as is shown by the following examples:—

At the Dowlais Works in South Wales the blowing-engines<sup>1</sup> are worked with a boiler pressure of 100 pounds per square inch, and have two steam cylinders side by side, one 36 inches in diameter for high-pressure steam, and another, which is steam-jacketed and 64 inches in diameter, for low-pressure.

Connected with and directly underneath each steam cylinder is a blast cylinder 88 inches in diameter. The engines are designed to give a maximum pressure of 10 lbs. to the square inch, and working with a 5-foot stroke at 23 revolutions per minute, give 19,000 cubic feet of air per minute at atmospheric pressure.

They are capable of blowing 25,000 cubic feet of air per minute if necessary, and the pressure actually developed is over 5 lbs. to the square inch.

At the Barrow Hematite Steel and Iron Company's works<sup>2</sup> a set of 3000 horse-power quarter-crank blowing-engines are used. The two steam cylinders together form a compound engine, which can be worked as condensing or non-condensing. The steam

<sup>1</sup> See T. M. Grant, "Notes on Blowing-Engines," *Journ. of the West of Scot. Iron and Steel Inst.*, vol. v. p. 128.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1903, ii. p. 628.

cylinders are 42 inches and 84 inches respectively in diameter, with a 5-foot stroke. The steam pressure is 150 lbs., and the normal speed is 50 revolutions per minute, which is equivalent to a duty of about 20,000 cubic feet of free air.

They can be worked at 80 revolutions per minute with a maximum pressure of 30 lbs. to the square inch.

For foundry purposes the blast is usually supplied by centrifugal fans or by blowers. The fan, although possessing the advantage of great simplicity, has but limited application, since it is useless when pressures exceeding about 6 inches of water-column are required to be produced. In such cases the Root's blower, or a machine of similar type, may be advantageously employed. It consists of an iron casing, in which are placed a pair of revolving cast-iron wafters driven by belts off pulleys, and making about 400 revolutions per minute, the smallest possible clearance being left between the two curved surfaces as they revolve. The blast is conveyed in air-tight riveted sheet-iron or steel pipes or *mains* of ample cross section to the hot-blast stoves.

As examples of more recently introduced forms of blowing-engines, gas-driven engines and steam turbines may be mentioned.

Large gas blowing-engines have been adopted with considerable success. The first blowing-engine worked by blast-furnace gas was erected at Seraing in 1899; it was of 600 horse-power, and was worked with unpurified gas.<sup>1</sup>

In recent years there has been a great development of the use of the surplus gases of the blast-furnace for the driving of gas engines to provide power, not only for the blowing-engines, but also for all purposes connected with ironworks, and this method is found to be more economical than the older methods using intermediary boilers, etc. In 1906 there were in work or in course of erection in Germany, in 41 smelting-works, no less than 349 gas engines, with an effective horse-power of 385,000, the great majority of these being worked with blast-furnace gas. One of the early difficulties met with in the use of blast-furnace gas in engines was the presence of dust and tar, considerable wear and tear resulting from the presence of gritty dust, owing to the want of efficient means of cleaning. The cleaning of the gases has therefore received a considerable amount of attention, and it is recognised that cleaning is also advantageous for that portion of the gas which is used in the hot-blast stoves. A. Sahlin<sup>2</sup> has described the methods used for cleaning the gases, and states that it should take place in three stages, viz. :—

1. The preliminary dry cleaning by means of dust-catchers, etc.
2. Further cleaning, so as to fit the whole of the gas for use in stoves, roasting-kilns, etc.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1900, i. p. 109.

<sup>2</sup> *Ibid.*, 1905, i. p. 324.



This is accomplished by means of stationary cleaners, and then by coolers or scrubbers, with or without the addition of revolving washers. The stationary cleaners consist of a combination of cylindrical vessels in which the gas is led downwards with a rapid motion and upwards with a slow motion. In the scrubbers the gases pass upwards while a spray of water falls from the top, thus wetting the particles of dust and assisting their separation. The interior of the scrubbers may contain sieves, coke, bricks, etc., to increase the surface.<sup>1</sup>

3. The special cleaning of such part of the gas as is to be used for power purposes.

This final purification is effected by some type of centrifugal

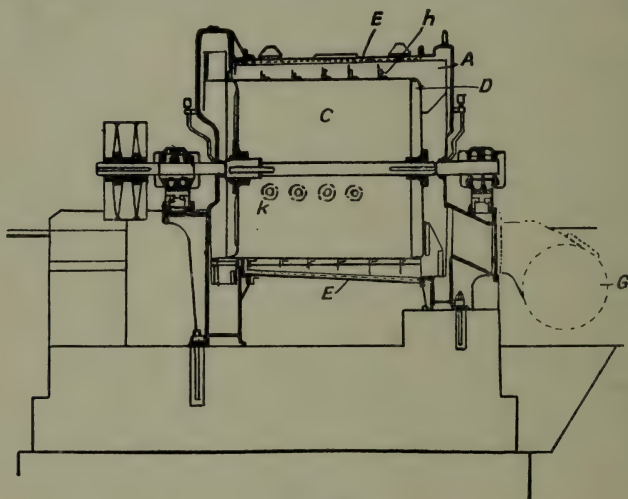


FIG. 175.

machine, such as that introduced by Theiren, shown in figs. 175 and 176.

This consists essentially of a rapidly revolving water-tight drum D, fig. 175, with vanes set obliquely on its periphery. This drum is surrounded by an outer fixed casing, which forms the suction-chamber A. This casing is lined with coarse wire netting E, so as to give a rough surface, and the clearance between the edge of the vanes and the inside of the casing is only about a quarter of an inch. Water enters at the side of the apparatus at K, tangentially to the casing of the middle chamber C, and leaves the apparatus through the pipe G, shown in figs. 175 and 176. The gas is drawn in by the vanes h, and the coarse dust separates in the suction-chamber. By means of fans at each end of the

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1906, iii. p. 45.



drum D, the gas is then drawn through the space between the drum and the casing, the dust is projected against the spiral meshes of the grating E, while the water entering at the same time is also distributed over the surface of the grating. In this way the water is broken up and the dust efficiently removed. This apparatus is capable of cleaning a blast-furnace gas containing 4 to 5 grammes of dust per cubic metre down to 0.008 gramme per cubic metre, which is actually more free from suspended particles than is the surrounding atmosphere. This result is obtained with less than half a litre of water per cubic metre of gas. Although this apparatus requires more power than a slowly revolving cleaner, it is found to be more efficient,

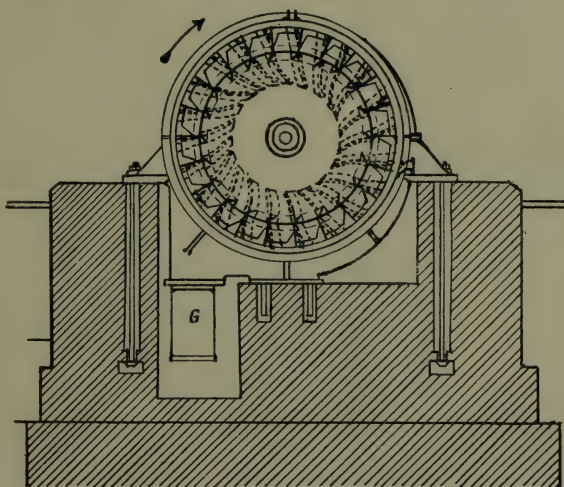


FIG. 176.

and to be specially suited for use where high purification is required.

Steam turbines have been introduced in the Cleveland district and elsewhere; they are said to work economically and to give a uniform and steady air-blast. The use of a turbine blower in connection with ordinary reciprocating steam blowers is considered in some respects to be the ideal method of augmenting an existing blowing-plant. Turbines have the advantage of being cheaper and smaller than reciprocating blowers.

**Hot-blast Stoves.**—The temperature of combustion increases with the temperature of the air consumed up to the limits which are fixed by dissociation. Hot air economises in the blast-furnace a sum of *calories* equal to that which it brings, but if this heat has to be initially imparted to the air by the combustion of a fuel of equal value to that consumed in the furnace, it is

evident that the economy will be at best but doubtful. In all cases the advantage of hot-blast will be in direct proportion to the cheapness of the fuel that is burnt in heating the blast. There is a great advantage when the waste heat of the furnace can be utilised in this way. By employing a fuel identical with that burnt in the blast-furnace it would appear, however, that there is still a distinct advantage due to the more perfect combustion of the carbon than is attained in the furnace, there being produced a greater proportion of carbonic anhydride as compared with that of carbonic oxide.

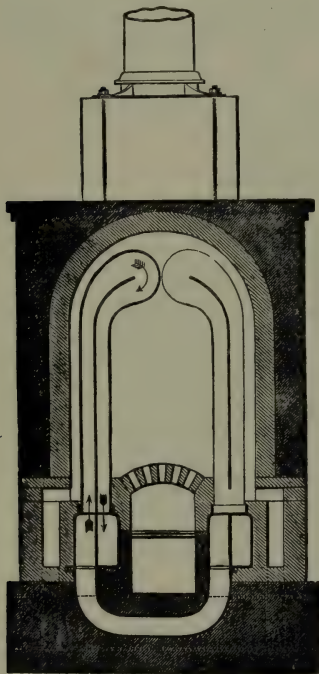


FIG. 177.

The apparatus in which the blast is heated before passing to the furnace was formerly heated by solid fuel, but now the waste gases from the furnace are practically always used. The first appliances for heating the blast date from 1828, when they were introduced by Neilson at Glasgow. This discovery, that 100 lbs. of coal burnt in heating the blast was able to save 300 or 400 lbs. of fuel burnt in the furnace, was received with disbelief, and ironmasters were very slow in availing themselves of one of the most important inventions which had been made in connection with the metallurgy of iron.

The cast-iron hot-blast stoves formerly used in metallurgical works may be referred to two types, both introduced at the same date. In 1833 Faber du Faur invented a hot-blast stove, consisting of sixteen cast-iron pipes united by semicircular

bends, forming one long serpentine pipe enclosed in a chamber heated by the waste gases from the blast-furnace. It was placed directly above the throat of the furnace. The second type of iron hot-blast stove differed from the former in that the blast-current was split in its passage through the stove. It consisted of an oblong fire-brick chamber, containing a series of  $\Lambda$ -shaped cast-iron pipes, that connected two parallel horizontal main pipes embedded in the masonry on either side of the rectangular fireplace that extended throughout the stove.

A modification of this second type is the so-called pistol-pipe

stove (fig. 177). In this case the arch is replaced by a single pipe divided longitudinally, the division reaching nearly to the top, which is enlarged in the form of the stock of a pistol.

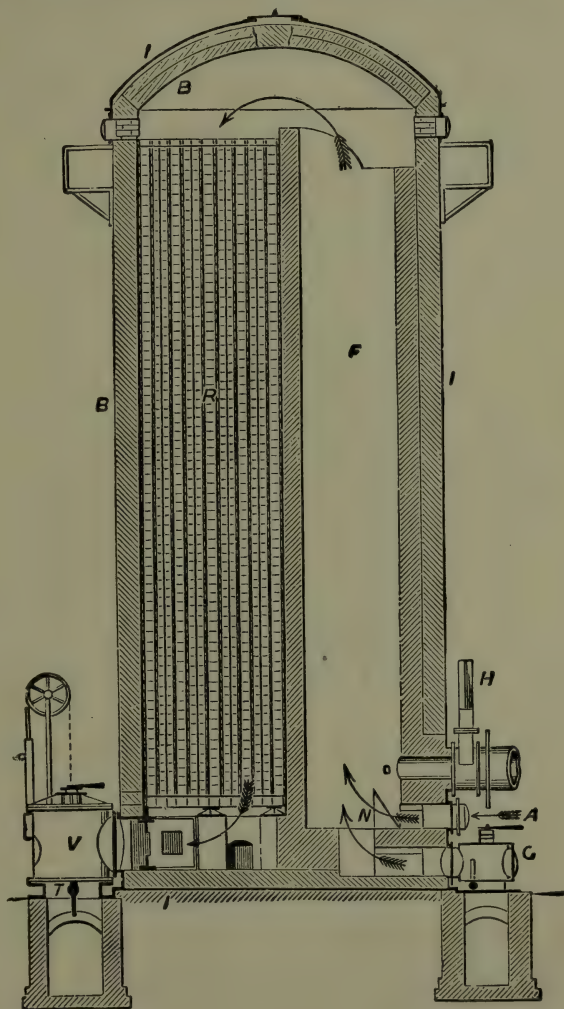


FIG. 178.

Two main types of regenerative hot-blast stoves are now employed. These are based on the principle of the intermittent absorption of heat by masses of fire-brick and the transference of the heat to the blast. The first stove of the first type was con-



constructed by Cowper in 1860; it is similar in arrangement to a Siemens regenerator. It is enclosed, however, in an iron case so as to withstand the pressure of the blast. The first stove of the second type was constructed by Whitwell in 1865 for the Thornaby Works at Stockton. It is essentially a serpentine pipe-stove constructed of fire-brick.

The Cowper stove, which is represented in sectional elevation and plan in figs. 178 and 179, consists of a sheet-iron tower I, of circular horizontal section, closed with a dome-shaped roof B, and lined internally with fire-brick. A circular flame-flue, F, extends from the base to the dome, whilst the remainder of the stove is filled with fire-brick chequer-work, and forms the regenerator R. The waste gases from the blast-furnace pass in by the valve G, and are burnt at N, the necessary air for com-

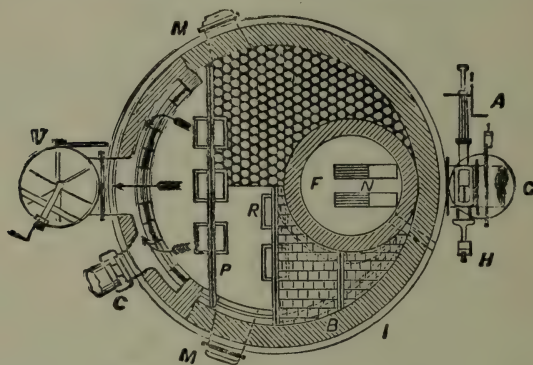


FIG. 179.

bustion entering by the valve A. The flame descends through the chequer-work and passes out by the chimney-valve V. In this way the brickwork becomes heated. The valves G, A, and V are closed, and cold blast, admitted through the valve C, is passed through in the reverse direction. It absorbs heat from the chequer-work, and is delivered as hot-blast by the valve H. The chequer-work is constructed of Cowper's honey-comb bricks. Two stoves are worked in conjunction, one being heated while the blast passes through the other. It is advisable to have a third in reserve. These stoves are 60 to 65 feet high, and 26 to 28 feet in diameter. Compared with pipe-stoves, the saving of fuel is about 20 per cent., and the increased make is also 20 per cent. An exact average of over 100 stoves shows the saving in fuel to amount to a little over 5 cwt. of coke per ton of iron.<sup>1</sup>

<sup>1</sup> E. A. Cowper, *Journ. Iron and Steel Inst.*, 1883, p. 576.



The Whitwell stove<sup>1</sup> is shown in fig. 180. It is merely a brick-work serpentine pipe formed by vertical walls, and enclosed in a cylindrical case. The waste gases from the furnace enter at A and are burnt, air being admitted through the passages *aa*. The flame passes up and down the passages formed by the dividing walls, and escapes to the chimney by the passage C. When the stove is heated, the gas and chimney valves are closed, and cold blast is admitted at D, and passes out heated at B. The walls forming the regenerator consist of 5-inch brickwork. The older forms of Whitwell stove were 25 feet in height. Recently

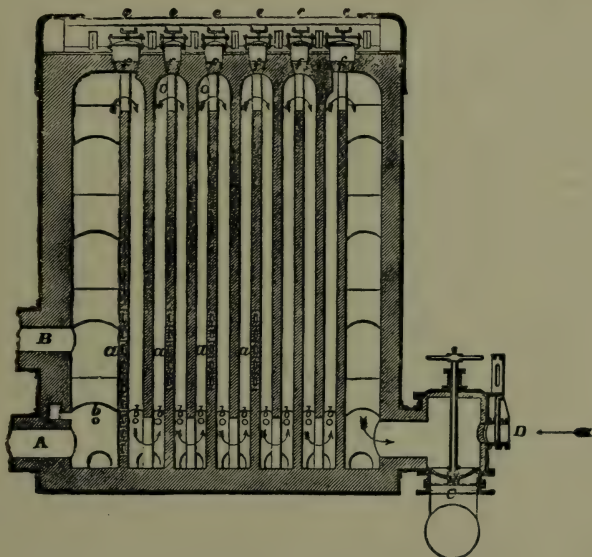


FIG. 180.

the height has been greatly increased, the largest size adopted being about 70 feet high and 25 feet in diameter. A domed top is also now used in place of the flat top as introduced by Whitwell.

A number of modifications have been introduced in the construction of fire-brick hot-blast stoves; for example, the Ford and Moncur stove,<sup>2</sup> first introduced in Cumberland, has been designed chiefly to facilitate cleaning. For this purpose the upper edges of the bricks employed are dormer-shaped, to prevent the dust lodging; the stove is also divided into four separate parts by vertical partitions, so that when it is desired to clean out the

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1869, p. 206; 1871, ii. p. 217.

<sup>2</sup> *Ibid.*, 1896, i. p. 201.

dust, the blast is turned on to each section separately, and by proper release-valves the air is allowed to suddenly escape, and so carry away the dust, and it is claimed by this means that the stoves can be kept clean without the necessity of stoppages.

In the Gordon-Cowper-Whitwell stove, used largely in the Southern States of America, both the Cowper and the Whitwell systems are combined, while a separate chimney is provided to make each stove quite independent of the draught of the stack. It is claimed that these stoves have the advantage that gases which contain a considerable proportion of dust may be employed, while, owing to the fact that the latter part of the regenerative action is conducted by Cowper bricks, the gases are efficiently cooled, and a high temperature can be imparted to the blast.

In the Massick and Crookes stove<sup>1</sup> the regenerator is on the Whitwell principle, but arranged in what is known as a "three-pass" system; the main combustion-tube is placed in the centre of the stove, and the gases, after passing up the central tube, pass once down and once up through gas-passages similar in principle to those of the Whitwell stove, but arranged concentrically round the main combustion-tube. The products of combustion pass out at the top of the stove.

**Dry Blast.**—The question of the effect of the moisture contained in the air supplied to blast-furnaces has received very much attention during the last few years, and is certainly of considerable importance in many localities.

As long ago as 1799 Mr Dawson of Low Moor read a paper before a scientific society in York, pointing out the great difference in the moisture of the air going into the blast-furnace in the hot months of the year and in the winter months; and it is also interesting to note that the Duke of Devonshire, in his address delivered in 1869 at the inaugural meeting of the Iron and Steel Institute, mentioned, among the important problems which at that time either seemed to have found solution or still remained to be solved, the effect of moisture contained in the air of the blast, and varying at different seasons of the year. It was at one time thought that in hot-blast practice the introduction of water vapour would be advantageous, as the hydrogen produced by its decomposition is such a powerful reducing agent.

The question was considered at length by Sir L. Bell, who came to the conclusion, in his *Principles of the Manufacture of Iron and Steel*, that there is no advantage to be obtained by increasing the quantity of water vapour in the blast.

W. H. Fryer considered the effect of moisture in the air-blast before the Cleveland Institution of Engineers in November 1890, and stated that the effect of the moisture is to lower the temperature at the tuyères so that more fuel and greater engine-power have to be used, and the variations in the quantity of moisture

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1890, ii. p. 340.

cause constant variations in the working of the furnace and in the nature of the iron produced.

In the same paper Mr Fryer gave drawings and particulars of an apparatus for drying the air, at a cost of 4½d. per ton of pig-iron produced. This apparatus, which does not appear to have been used on more than an experimental scale, consisted of a cast-iron cylinder fitted with shelves, on which were placed lumps of dry calcium chloride which it was proposed to dry by heat after being used for a certain time; the apparatus was arranged so as to work continuously. Calorimetric calculations are given, based on data given by Sir L. Bell with regard to hot blast, and the reactions in the furnace, showing the losses due to the moisture in the blast. The results with dry blast at 10° C. and 485° C. are most interesting in view of recent developments, and are as follows:—

Temperature of blast . . . . .	10° C.	485° C.
Increase of make of pig-iron per cent. . . . .	31·42	15·07
Diminution of power required for blast per cent. . . . .	67·50	15·71
Diminution of coke required in furnace . . . . .	21·51	12 01

In 1899 S. D. Mills<sup>1</sup> called attention to the necessity of using the driest air possible for supplying blast-furnaces. He had found great differences in the amount of moisture in the air inside and outside the engine-house on a cold day, and suggested that the buildings and engines should be arranged so as to take air directly from the exterior in preference to using the air in the buildings.

The application of dry blast to the manufacture of iron has been practically worked out by J. Gayley<sup>2</sup> who points out that the air used in the blast-furnace is by far the most variable element involved in the process; for whereas the raw materials used for the charge vary within about 10 per cent., the atmosphere, of which large quantities are used per ton of iron made, varies in its content of moisture from 20 to 100 per cent. from day to day, and often in the same day. The desiccation of the air used in blast-furnaces in such a way as to reduce its moisture to a small quantity and to keep it uniform must of necessity contribute in a marked degree towards the attainment of uniformity in the furnace operations.

With air containing 1 grain of water per cubic foot, there is passed into the furnace, for each 1000 cubic feet used per minute, practically 1 gallon of water per hour. A furnace of average size in the Pittsburg district consumes about 40,000 cubic feet of air per minute, which would pass into the furnace 40 gallons

<sup>1</sup> *Journ. of the U.S. Association of Charcoal Iron Workers*, vol. viii. pp. 306-310.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1904, ii. p. 275; 1905, i. p. 256. See also *Amer. Inst. Min. Eng.*, Feb. 1906.



of water per hour for each grain of moisture contained in a cubic foot of air.

The results of observations of the amount of moisture contained in the atmosphere at Pittsburg are given by Mr Gayley in the paper mentioned above, which show that the amount varies from 1 grain per cubic foot on an exceptionally dry day in winter, to over 10 grains per cubic foot on an exceptionally humid day in summer. There would therefore, on these two days, enter the furnace 40 and 400 gallons of water per hour respectively.

After many preliminary experiments, Mr Gayley decided that the most practical method of desiccating the air was refrigeration by means of anhydrous ammonia. For this purpose an insulated chamber containing coils of pipe is used; this chamber is so located that the air for the blowing-engine is drawn through it at atmospheric pressure. The brine system of refrigeration is used, the ammonia machines for cooling the brine being of the compressor type. As the air passes through this chamber on its way to the blowing-engine the moisture present is condensed as water or as frost on the lower pipes, and as frost or ice only on the upper pipes. When the pipes have become covered with frost, the cold brine is shut off from several vertical lines of coil at once and warmer brine is passed through these pipes.

The frost is rapidly melted and the water formed run off; cold brine is then again run through the pipes which have thus been cleared of frost, and the refrigeration and desiccation again commences. For cooling the calcium chloride brine used in the refrigerators, brine tanks are used which contain twenty coils of pipes, consisting of an inner and an outer pipe, these coils being covered with the brine. The return brine from the refrigerating chamber flows into the top of the tank, is cooled by the ammonia expanding between the outer and the inner pipes, withdrawn by a pump and forced through the inner pipe (where it is cooled below  $0^{\circ}$  C.), and thence into the coils in the refrigerating chamber.

This system of brine refrigeration was used in order to minimise the risk of accidents which might occur should direct refrigeration by means of ammonia be used.

For thawing off the frost from the coils, these are divided into three divisions, and one of these is thawed off as above every day; in this way refrigeration is not interfered with. During the first run of the plant the water collected from the thawing of the frost averaged 2784 gallons per 24 hours.

It should be remembered that advantages accrue not only from the fact that a large amount of moisture is actually extracted, but also from the fact that the air used is practically uniform in moisture content, in spite of constant variations in the humidity of the atmosphere. The very first run obtained by Mr Gayley after the erection of the desiccating plant showed great saving in the fuel consumption, and also an increased burden.



The effect of thus cooling the blast is also to increase the effective capacity of the blowing-engines, owing to the greater density of the air.

The following figures given by Mr Gayley illustrate the differences obtained in the working of a furnace :—

	With Ordinary Blast.	With Dry Blast.
Product . . .	358 tons per day.	447 tons per day.
Coke . . .	2147 lbs. per ton.	1726 lbs. per ton.

B. Ossan<sup>1</sup> considers that dry blast is especially suited for a climate where the variations between day and night temperatures are considerable. In Europe, the changes are not so marked as at Pittsburg, and Ossan is of opinion that Gayley's methods would not show here a sufficient saving of fuel to pay a satisfactory return for the capital invested in the plant. By modifications in the plant, however, the cost could be much reduced, and it would be sufficient in most cases if a uniform humidity were maintained throughout the year without removing practically the whole of the moisture, as was done in the original Gayley's plant at Pittsburg.

J. E. Johnson, jun.,<sup>2</sup> has considered the relative cost of the different methods of air refrigeration, and is of the opinion that the use of a brine-circulating system, as used in Gayley's original plant, as a precaution against accidents, is unnecessarily expensive, whilst the substitution of the direct expansion of the ammonia would reduce the first cost, the labour and the power required. He also suggests the use of a two-stage method of refrigeration, one at, say, 36° F., and the second at 15° F., and also urges that there is no commercial gain by refrigerating at too low a temperature.

<sup>1</sup> *Iron Age*, 1906, vol. lxxviii. p. 798.

<sup>2</sup> *Journ. Iron and Steel Inst.*, 1906, iii. p. 404.

## CHAPTER XI.

### THERMO-CHEMISTRY.

THE great importance of thermo-chemistry in relation to metallurgy is so evident that it is absolutely necessary for the student to have such knowledge as will enable him to consult with advantage the original memoirs of Andrews, Berthelot, Julius Thomsen, Nernst, and others. In this country comparatively little attention has been devoted to thermo-chemistry in relation to metallurgical teaching, but in France admirable work has been done, notably by Ditte,<sup>1</sup> in bringing within the reach of students the results of the labours of Berthelot and of St Claire Deville.

Ostwald reminds us that chemical energy is the least known of all the various forms of energy, as we can measure neither it nor any of its factors directly; the only way of obtaining information regarding it is to transform it into another species of energy. It passes most easily and completely into heat, and the branch of science which treats of the measurement of chemical energy in *thermal units* is called thermo-chemistry. The quantities of heat evolved or absorbed measure the decrease or increase of chemical energy in so far as other energy is not involved in the process. The ordinary equation of the chemist  $C + O = CO$  is far from representing the whole truth, for in fact C unites with O to form an entirely new body (CO), which may be liquid, solid, or gaseous, but it never has the same potential energy as was possessed by the bodies from which it was formed. The equation should therefore be  $C + O = CO + q$  *heat units*.

It must be remembered that only the final result of a chemical process can be measured. The calorimeter is the instrument used in thermo-chemical measurement. First as regards the "calorie" employed. The student will remember that the calorific power of carbon in the form of charcoal as determined by the aid of the calorimeter is given on p. 248 as being 8080, that is, 8080 units (grammes) of water will be heated from 0° to 1° by the complete combustion of 1 unit (1 gramme) of carbon. The calorie hitherto

<sup>1</sup> *Leçons sur les Métaux*, Paris, 1891.

employed in this book is, however, too small for use in thermo-chemical measurement. The heat required to raise 1 kilogramme of water is the unit employed in this chapter. It must be borne in mind that *the quantities of energy and heat given in thermal equations refer to such quantities of the substances as amount to their formula weight in grammes.*

Hence the thermal equivalent of carbon burnt to carbonic anhydride is 97. The calorific power of charcoal being 8080, it may be well to show how the number 97 is deduced. In the equation  $C + 2O = CO_2$ , 12 grammes of carbon (its equivalent weight) are used. 8080 represents the unit of carbon, hence  $8080 \times 12 = 96,960$ ; but the thermo-chemist, as above stated, employs 1000 grammes as the unit of water instead of 1 gramme, and the sum becomes  $\frac{96,960}{1000} = 96.960$ , or in round numbers, 97.

The various forms of calorimeter are fully described in the works to which reference is given at the end of this chapter. The form of the calorimeter is modified to suit the particular conditions of the experiment, but the limits of this book will only permit a brief reference to the methods by which the calorimetric determinations given in the accompanying table were made. (See Folding Plate placed at the end of this chapter.)

The calorimeter employed by Berthelot is a thin cylindrical vessel of platinum, of about 600 c.c. capacity. If, for instance, the problem is to determine the heat evolved by the reaction between two liquids, these would be placed in flasks of very thin glass of about 300 c.c. capacity, provided with short necks, marked with the calibration line at the base of the neck. These receptacles are allowed to stand near the calorimeter until they acquire a constant temperature, which is carefully measured. The difference in temperature between their contents should not exceed  $\frac{1}{10}$ th of a degree. The contents of one flask would then be poured into the inner chamber of the calorimeter and rapidly stirred with the thermometer, the temperature is then noted, and the contents of the second flask are added to the liquid already in the calorimeter, and careful thermometric observation is made to ascertain whether the admixture has been attended with a lowering or an elevation of temperature. The above description has merely been given to indicate the general nature of the method, but treatises on calorimetry must be consulted with reference to the precautions to be observed when solids and liquids react, or when the reaction between gases and liquids has to be studied.

**Bomb Calorimeter.**—The instrument of which a description will now be given is the one in use at the Royal School of Mines. It often happens that the metallurgist has to deal with reactions which are attended with vivid combustion—the reaction, for instance, between solids and gases—the product of which is

gaseous, and in such cases closed combustion-chambers are employed, and the heat is not measured directly by a thermometer, but is transferred, through the walls of the combustion-chamber, to water contained in a receptacle in which the combustion-chamber is placed. There are various forms of such combustion-chambers, but the one most serviceable to the metallurgist is the modification of Berthelot's bomb calorimeter devised by M. Mahler, and the following description shows the nature of the appliance and the method of using it. The apparatus consists essentially of a shell or bomb B (figs. 181 and 182), forged out of high-class mild steel, having a capacity of 654 c.c. (say 40 cubic inches), and weighing about 4 kilogrammes (or  $8\frac{4}{5}$  lbs.) with its accessories. The shell B, which is 8 millimetres

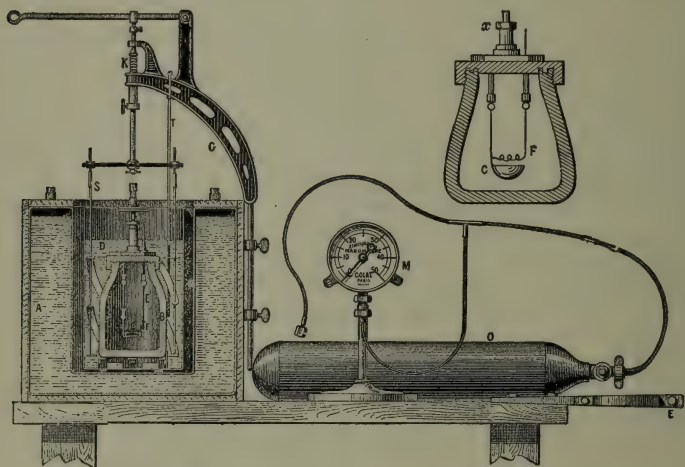


FIG. 181.

FIG. 182.

( $\frac{5}{16}$ -inch) thick, is nickelised on the outside, and enamelled inside, so as to withstand the corrosive and oxidising action of combustion, but the coating of enamel does not sensibly interfere with the transmission of heat. The shell is closed by a screw cap, tightened on to a lead ring; and the cap is provided with a conical screw cock (*x*, fig. 182) for the introduction of oxygen. A platinum rod, attached to the cap, holds the capsule C, on which is placed the fuel to be tested, and the latter is ignited by being brought in contact with a spiral of iron or platinum wire F, heated by an electric current. It may be well to assume that the material is either carbon or hydrocarbon, which is to be burnt in oxygen.

The sample to be tested is introduced into the steel bomb, which is then closed, and charged with oxygen under pressure,



and the whole apparatus is immersed in the water of the calorimeter. If the fuel be then ignited by the aid of a wire heated to redness by an electric current, it will burn completely and almost instantaneously, the water formed by the combustion of the hydrogen being condensed on the inside surface of the bomb. The heat disengaged by the explosion is transmitted to the water of the calorimeter, and may easily be estimated. The pressure of oxygen is determined by the condition that combustion must always be complete, and that an excess of oxygen is indispensable.

For testing a solid or liquid fuel, a gramme of the substance is placed in the capsule and the cap is screwed down tightly. Oxygen, under pressure, is allowed to enter by the cock, until the manometer M shows that a suitable pressure is obtained, generally from 20 to 25 atmospheres. Care must be taken, especially with coal in a finely divided state, to prevent the sample from being displaced, in which case there would be danger of part escaping combustion, and for this reason the sample is generally compressed into a pellet. The shell thus prepared is placed in the calorimeter D, which contains a known quantity of water, when the thermometer T is adjusted, and the helicoidal agitator S set to work for a few minutes to bring the whole apparatus to the same temperature, when all is ready for the observation. In order to prevent irregular loss of heat by the calorimeter D, it is placed upon three small pieces of cork within a large, metallic, double vessel of water A, covered externally with a thick layer of felt and provided with a thermometer. This vessel serves also as a support for the bracket G, from which the stirrer S is suspended, and to which the handle and spring K, for working the stirrer, are fixed. O is the vessel containing the supply of oxygen, and E is a clamp in which the bomb may be fixed and prepared for the experiment.

The temperature is noted every minute for four or five minutes, and then the charge is fired by electricity. Although the combustion is almost instantaneous, the transmission of heat to the water requires a few minutes. The temperature is noted, first half a minute, and then one minute, after the ignition, and afterwards every minute until the thermometer begins to fall, which shows that the maximum temperature has been reached, after which the observations are continued for about five minutes more. The principal elements of the calculation are thus afforded, and especially the one correction necessary, which is due to the loss of heat sustained by the calorimeter before reaching the maximum temperature. The agitator S must be worked regularly during the observation, at the conclusion of which the shell is removed from the calorimeter, the cock is opened, and then the shell itself. The inside of the shell is washed with a little distilled water, so as to collect the acid liquid

formed during the explosion. The amount of acid is determined by titration.

It is advisable, when experimenting on substances poor in hydrogen, like coke, and consequently incapable of furnishing by combustion sufficient water to form nitric acid, to put a little water at the bottom of the bomb.

For determining the calorific value of a gas of constant volume, a vacuum is made in the bomb, the exact cubic contents of which is known. The bomb is filled with the gas; a fresh vacuum is produced by exhaustion until the pressure is only a few millimetres of mercury, and the bomb is filled with the gas at the atmospheric pressure and temperature of the laboratory, and the operation is completed in the same manner as with solid and liquid fuels.

The significance of the thermal data given in the table facing page 404, which has been obtained by one or other of the calorimetric methods, will now be considered.

It is assumed that the student is familiar with the theory of the granular structure of matter, and with the molecular theory of gases. He must also know that the atoms of every element have valencies of their own, and, further, that there may be distinct movements and reactions between the atoms arranged in a molecule. The question naturally arises—Why do certain reactions take place, while others do not? Berthelot held “that every chemical change which can be accomplished without the aid of a preliminary action or the addition of energy from without the system necessarily occurs if it is accompanied by a disengagement of heat.” Viewing a reaction generally, he held that if external energy is not imparted to a system, the tendency will be to form that compound the production of which is accompanied by the evolution of the maximum quantity of heat. It is true that changes resulting in a positive calorific effect occur more often than those accompanied by negative ones, but it is well known that, of two or more possible reactions, the one which is accompanied by the evolution of most heat is not always the one which actually occurs. Decompositions accompanied by negative calorific effects are more frequent at high than at low temperatures. In this connection it must be remembered that heat is not the only form in which energy can be lost by a changing chemical system, as the change may give rise to electrical phenomena. A redistribution of atoms in the molecule may take place; and although the energy is not lost to the system, it may not be possible for it to directly appear as heat. In some cases the only outward sign of change is the passage of an element from a normal to an allotropic modification.

Van't Hoff<sup>1</sup> has pointed out that modern chemical theory had two weak points: it expressed itself neither as to the relative

<sup>1</sup> *La Chimie dans l'espace* (original edition).

position of the atoms nor as to their movement. It is known that many active organic bodies lose their activity by being heated; and this fact, which is recognised as being of much importance in organic chemistry, can hardly be without significant relations in the inorganic reactions with which the metallurgist has to deal.

The atoms in the molecule have, as has already been stated, movements of their own; and, as Lotther Meyer has urged, "if these movements of the atoms are to be considered, then we must investigate what part in the observed calorific effects is to be attributed to them, and how much is due to the potential energy of the hypothetical force of affinity. It is doubtful, however, whether the atoms do possess powers of attraction, and consequently potential energy; it is more probable that the whole of the kinetic energy the atoms give out is already their own as such." But suppose atoms do possess "potential energy" of their own to which they owe their "affinities," then when the system undergoes change which satisfies the affinities of the atoms without the addition of energy from an external source, this change must be attended by a "locking up" of energy which must have been kinetic, and consequently there is less kinetic energy available in the system to appear as heat, so that, although in a particular reaction but little heat may be evolved, there may nevertheless be a considerable degradation of chemical energy.

In chemical operations generally, and especially in metallurgical ones, there is another consideration of much importance. If two compound bodies react one upon the other, the presence of the products of the reaction will bring it to an end, and a state of equilibrium will be established, so that both the original and the newly formed substances are present in definite quantities that remain the same so long as the conditions of temperature and pressure do not undergo further change. If this is the case, the reaction can only be resumed if the products are eliminated from the system as fast as they are formed. In "wet" chemical processes this removal is effected by the precipitation of a product, or by its evolution as a gas. In metallurgical operations conducted by the aid of fire the products are often gaseous, and are swept away by the draught of the furnace. In other cases the fusion of the products enables this separation to be effected, as the products either flow away or arrange themselves in layers under the influence of gravity.

Again, in very many metallurgical processes, reactions are rendered incomplete by the limitations imposed by the presence of bodies which cannot be speedily eliminated from the system, and the result may be to greatly retard the completion of an operation. The time has come when the principles of dynamic chemistry must be applied to the study of metallurgical problems



if they are to be correctly understood, and it is, moreover, necessary to remember the part played by the surface separating the different aggregates in contact with one another. When, for instance, a reaction has to take place accompanied by the evolution of gas, there must be space into which the gas can pass, and the rate at which change takes place will obviously depend on the state of division of the mass.

One of the most remarkable points in the whole range of chemistry is the action engendered between two elements capable of reacting, by the presence of a third body. It may be that merely a trace of a third body is necessary to induce reaction, or to profoundly modify the structure of a mass. H. Le Chatelier and Mouret have pointed out that in certain cases it is inaccurate to say that the third body causes the reaction to take place, because, after it has destroyed the intermolecular resistances which prevented the reaction taking place, the third body ceases to intervene. This is apparently the case when platinum sponge effects the union of oxygen and hydrogen, or, conversely, when very hot platinum splits up water vapour into its constituent gases. Future investigation will, it is to be hoped, show whether the platinum does not exert some direct action in such cases. We can no longer neglect the study of such questions from the point of view of their practical application. The manufacture of red-lead presents a case in point. In "drossing" molten lead, the oxidation of the lead is greatly promoted by the presence of a trace of antimony, and, conversely, in the separation of silver from molten lead by the aid of zinc, H. Roessler and Endelmann have shown that aluminium has a remarkable effect in protecting the zinc from loss by oxidation, and, further, the presence of one-thousandth part of aluminium in the zinc is sufficient to exert this protecting action on that metal.

An examination of the following thermal equations and the remarks which precede them will show how frequently, in conducting metallurgical operations, demands are made upon energy, in the form of heat, from a source external to the particular "chemical system" which is undergoing change. It has been urged that if it is the energy of the external heat which dissociates a compound, and enables a reaction to take place, then chemical equilibrium such as is revealed by experiments on dissociation is really equilibrium between the energies of affinity and of heat. It follows, as M. Duhem<sup>1</sup> has pointed out, that the third law of thermo-chemistry is greatly weakened, if not rendered absurd, by the necessity for bringing external heat to a chemical system. This law states that "Every chemical change which is accomplished without the intervention of external energy tends towards the production of a body which evolves the most heat." If it be necessary to import external heat, the law admits of being reduced

<sup>1</sup> Duhem, *Introduction à la Mécanique Chimique*, Paris, 1893, p. 79.



to the useless expression, "Every reaction which does not absorb heat evolves it."

But the more ardent members of the school of Deville, which rendered such splendid services to metallurgy and to physics, did not advocate the employment of the mechanism of atoms and molecules in dealing with chemical problems, but simply accumulated evidence as to the physical circumstances under which chemical combination and dissociation take place. They did not even insist upon the view that matter is minutely granular, but, in all cases of change of state, made calculations on the basis of work done, viewing "internal energy" as a quantity which should reappear when the system returns to the initial state; and they viewed chemical combination and dissociation as belonging to the same class of phenomena as solidification, fusion, condensation, and evaporation. As yet, the study of chemical equilibrium is not sufficiently advanced to afford a basis for building a theory of metallurgy; and if there is evidence of the existence of atoms and molecules, it is not advisable to ignore their existence when dealing with metallurgical problems.

There is one important theorem developed by M. Moutier which must not be overlooked. He has shown that under a given pressure there is only one temperature at which transformations are reversible. If the conditions of equilibrium are such that the transformation occurs below the critical temperature, it is attended with evolution of heat, while, on the other hand, if the transformation occurs above this temperature, it is attended with absorption of heat. Take the case of a mixture of carbonic anhydride, lime, and calcium carbonate, exposed to such a pressure and temperature that the system is in equilibrium. It is stable; more carbonic anhydride cannot combine with the lime, nor can fresh calcium carbonate be decomposed. But destroy the equilibrium by an elevation of temperature, carbonic anhydride and lime will be the result, but the reaction is attended with absorption of heat. On the other hand, destroy the equilibrium by lowering the temperature, lime and carbonic anhydride will combine, and the reaction will be attended with an evolution of heat. According to this law, the occurrence of a definite chemical change will not be determined by the fact that much or little work would be done (law of maximum work), but by the relation between the temperature and pressure to which the substances are subjected. This and other theorems of Moutier apply, however, only to reversible reactions, and the student should be warned that the theorems as to the conditions of chemical equilibrium lead in many cases to the expectation of reactions or transformations which are not found to occur exactly as anticipated. Thus reactions occur suddenly at an abnormally high temperature, and with explosive violence, whilst the theory of chemical equilibrium indicates that reactions should tend to check themselves, and that, therefore, there should

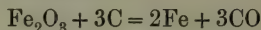
be no tendency to explosion. Other cases are presented by the phenomena of surfusion, supersaturation, and delayed ebullition. It would thus appear that a position of *unstable* or *false* equilibrium may be established; but if the equilibrium be destroyed, it may be by a further rise in temperature, by the presence of a minute trace of impurity, or even by a mechanical shock, the change is propagated rapidly through the mass.

Thermo-chemists are reproached for having neglected the study of reactions at high temperature, for the measurement of which, until recently, no simple methods were available, but now, as has been shown in these pages, that high temperatures can be measured with facility, it is to be hoped this reproach may be removed. When this is done, it will be interesting to compare the new thermal equations representing reactions at high temperatures with those now in use. Such an investigation will be very tedious, but there are many reactions at high temperatures the study of which can be undertaken, though they present great difficulty.

The student may fairly ask why a series of equations are presented which are confessedly based on numbers that were obtained from experiments conducted at temperatures differing from those employed in practice. The answer is that these equations do enable him to know the quantity of heat that will be required to obtain a certain result, and also indicate the probable temperature at which an operation can be effected. A reaction, the final result of which is represented by a minus number which is large when considered in relation to the quantity of material involved, generally means that a high temperature is necessary to effect it, but much will depend upon the melting-points of the members of the particular chemical system.

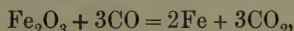
A reaction between sulphide of lead and sulphate of lead is attended with a large absorption of heat ( $-180$  large units), the mass involved being considerable. The reduction of ferric oxide by carbon is attended with an absorption of heat ( $-112$  large units). Both these reactions require very high temperatures; the mass in the latter case is relatively small, but the melting-point of the reduced iron is high.

The ordinary atomic equation



shows that the reduction of one ton of ferric oxide should be effected by four and a half hundredweights of carbon, leaving the CO produced to reduce still more ferric oxide. The thermal equation, with its very large minus number ( $-122$ ), prepares the student for the fact, well known to the blast-furnace manager, that the reduction of one ton of ferric oxide in accordance with the above equation is a very difficult operation, which would require a large amount of fuel; and, moreover, the student is led to expect

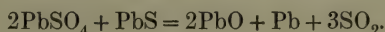
that the reaction represented by the above equation is evidently not the one that does happen, for he will see that the reaction—



which is accompanied by a disengagement of heat (+4·6), is probably the main reaction that takes place in the blast-furnace.

Whenever an equation shows that a reaction is accompanied by the evolution of much heat, it is safe to conclude that it will take place either at a low temperature or will be effected with ease.

**Thermal Equations.**—In using these, the student must bear in mind that all compounds that have to be decomposed will absorb as much heat during decomposition as they evolved while they were being formed, so that it is necessary to take the algebraic sum of each side of the equation, and to algebraically subtract the total heat required to effect all the decompositions from the total heat evolved from all the combinations. The difference will be the total quantity of heat evolved or absorbed, according to its particular sign. If the answer has a plus sign, then there is an evolution of heat; if a minus one, then there has been absorption of heat. For example, take the following equation:—



Here two molecules of lead sulphate and one molecule of lead sulphide have to be decomposed, whilst two molecules of lead oxide and three molecules of sulphurous anhydride are formed. Then

Total Heat required for Decomposition.

$$\text{PbSO}_4 \quad 2 \times 216\cdot2 = +432\cdot4$$

$$\text{PbS} \quad 1 \times 17\cdot8 = +17\cdot8$$

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$$+450\cdot2$$


---

Total Heat evolved by Combination.

$$\text{PbO} \quad 2 \times 51\cdot0 = 102$$

$$\text{SO}_2 \quad 3 \times 71 = 213$$

---


$$+315$$


---

$$\text{Total heat evolved by the members of the system} = +315\cdot0$$

$$\text{Total heat originally evolved when the members of the old system were formed} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} = +450\cdot2$$

$$\text{Difference, or the quantity of heat as would be measured by the calorimeter} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} = -135\cdot2$$


---

It will be seen that this reaction is accompanied by an absorption of heat, and is thus endothermic.

But it must be remembered that this calculation, to be rigorously accurate, ought to be corrected to the exact temperature at which the reaction occurs. The folding plate gives the



numbers obtained by heating up the chemical system to the temperature at which reaction occurs, then allowing the reaction to take place, and subsequently cooling the system to the initial temperature. Unfortunately, sufficient data as to the specific heats of various bodies at high temperatures have not as yet been accumulated to enable this to be done, but the correction to be made is as follows :—

Let  $M_1, M_2$ , etc., be the respective masses of the reacting bodies,

$M_a, M_b$ , etc., be the respective masses of the products of the reaction,

$S_1, S_2$ , etc.,  $S_a, S_b$ , etc., be the mean specific heats of the different masses, over a range of the temperature,  $t$ , of the water in the calorimeter to the temperature,  $T$ , of reaction,

$T$  = the "temperature of reaction," or that temperature at which the reaction can proceed,

$N$  = number of heat units as measured under the standard conditions in the calorimeter,

and let  $C$  be the true value required.

Then  $C = N + (T - t) [(M_1 S_1 + M_2 S_2 + \text{etc.}) - (M_a S_a + M_b S_b + \text{etc.})]$ .

In turning to the modern aspects of metallurgical practice, we shall see that the whole range of the metallurgist's field of study is changing. It is no longer possible for him to devise a series of operations on the evidence afforded by a set of equations which indicate the completion of an operation; he has, as has already been suggested, to consider the complicated problems which have been introduced into chemistry from the sciences of physics and mechanics. He has, in fact, no longer to deal merely with atoms and molecules, but with the influence of mass. If metallurgists are to advance their industrial practice, they must think in calories, and thus supplement the ordinary atomic "tools of thought." They will then be able to suggest what reactions can, under given conditions, take place; to indicate those which will be completed; and to avoid those that are impracticable.

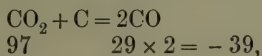
In order that the application of the preceding observations may be evident, it will be well to consider briefly the two main operations upon which metallurgical practice is based.

These are (1) the reduction of oxides by carbon and by hydrogen (see *ante*, p. 315), and (2) the oxidation of metals by an oxidising agent, usually air (*ante*, p. 312).

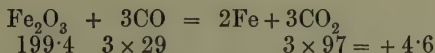
First, as regards the reducing action of carbon, it has already been shown that the heat of combination of carbon and oxygen into carbonic anhydride,  $\text{CO}_2$ , is 97 *large* calories, but in the blast-furnace, in the presence of excess of carbon, carbonic anhydride is converted into the main reducing agent, carbonic oxide, by the very well-known reaction  $\text{CO}_2 + \text{C} = 2\text{CO}$ .



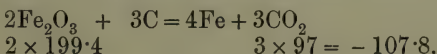
The carbonic anhydride, in combining with carbon to form carbonic oxide, becomes doubled in volume. If, however, the equation be completed by the addition of the thermal equivalents



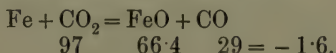
it will be seen that this reaction—one of the fundamental ones in the whole range of metallurgy—is really accompanied by an absorption of heat; that is, it is **endothermic**, and would, by Berthelot's law, be impossible if heat external to the chemical system were not available. In the blast-furnace there is such external heat, which acts in two ways: (1) by "depolymerising"—that is, simplifying the atomic constitution of the carbon, which can then combine with the oxygen of the  $\text{CO}_2$ , with evolution of more heat than from carbon in its normal condition; or (2) by dissociating the carbonic anhydride, thus setting oxygen free which is in a specially favourable condition to combine with the carbon, and so form the main reducing agent, carbonic oxide. In the case of the reduction of iron, the reaction



is **exothermic**, that is, attended by evolution of heat, but there is another reaction in which solid carbon plays a part,



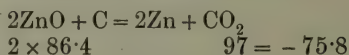
This is strongly endothermic; how, then, can the reduction of oxide of iron by the occurrence of this reaction be explained? The calorific power of carbon varies with its mode of aggregation; in the diamond form it evolves 94 calories in burning to  $\text{CO}_2$ , while the amorphous variety yields 97 calories. It may be the heat of the furnace depolymerises the carbon; and if it is brought to such a molecular condition that the heat of formation of carbonic anhydride from it is 117 instead of 97, then the endothermic equation would become an exothermic one. This is not at all an extravagant supposition, for it has been estimated that if carbon could be burnt as gaseous carbon, the heat of formation of carbonic anhydride would be no less than 136·0. We have, moreover, no knowledge, as yet, of the molecular form of the liberated iron. There is, however, another point to be considered: metallic iron will, as is well known, decompose carbonic anhydride, becoming oxidised itself, and forming carbonic oxide. The equation is



It will be seen, on comparing this with the last equation but one, that the amounts of heat are very nearly balanced, +4·6 in the

one case and  $-1.6$  in the other; and when this is the case, the inverse reaction may very readily be brought about by comparatively slight variations in the external conditions.

Two interesting cases may be borrowed from the metallurgy of zinc and of lead respectively. The reaction



occurs in the presence of excess of carbon, which splits up the carbonic anhydride formed; but it is strongly endothermic, as is also the reaction  $\text{ZnO} + \text{CO} = \text{Zn} + \text{CO}_2 = -18.4$ : the latter is, however, less endothermic than the former. It is nevertheless the fact that when zinc oxide and carbon are introduced into a retort which is strongly heated, zinc is reduced in abundance (this is the main method adopted in the metallurgy of zinc), carbonic anhydride together with some carbonic oxide being the result. How is this reduction to be explained? Possibly the carbon, under the influence of external heat, loses its condensed form and assumes one analogous to that in which carbon exists in carbonic oxide, so that during the passage from the system  $\text{ZnO} + \text{C}$  to  $\text{CO} + \text{Zn}$  all the heat is absorbed. The part played by the external heat is twofold: it furnishes the energy necessary to depolymerise the carbon, it may also modify the specific heats and heats of formation of the bodies in presence of each other. Dissociation also plays an important part (*see ante*, p. 393).

It will be evident that of the two reactions given above, the one in which carbonic oxide and oxide of zinc react is endothermic ( $-18.4$ ), but less so than that in virtue of which carbon acts on the zinc oxide ( $-75.8$ ). The passage from one set of reactions to the other may be effected by the presence of even a minute quantity of air entangled in the mixture of ore and carbon introduced into the retort. First, the oxygen in the air may form with the carbon some carbonic anhydride, and then some carbonic oxide, which reacts on the oxide of zinc. The carbonic anhydride,  $\text{CO}_2$ , which is the product of this reaction, is again converted by the excess of carbon present into carbonic oxide. The carbonic anhydride yields double its volume of carbonic oxide; hence the accumulation of carbonic oxide is very rapidly effected, even though its production originated in only a "trace" of air, an important factor in the mechanism of reduction.

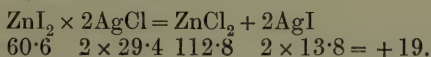
A state of equilibrium between the zinc oxide and carbonic anhydride does not become established, because carbonic anhydride is dissociated at the high temperature which exists.

Oxide of lead heated with carbon gives only carbonic anhydride; in fact, the reaction  $2\text{PbO} + \text{C} = 2\text{Pb} + \text{CO}_2$  is so slightly endothermic that but little external aid is needed to change the conditions and render the reaction exothermic.

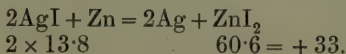
With regard to endothermic reactions generally, Victor Meyer

gives a word of warning. He says<sup>1</sup>: "Decompositions accompanied by negative calorific effects are more frequent at high than at low temperatures. This fact is usually expressed by saying that the heat represents the work necessary for the decomposition of the compound, or yields the kinetic energy required, which in the decomposition is converted into potential energy. A fundamental difference between decompositions requiring a red heat and associated with a negative calorific effect, and those taking place at the ordinary temperature, does not exist; for in both cases the particles of the materials possess kinetic energy, a part of which, with consequent lowering of the temperature, is utilised in bringing about the decomposition. It is therefore at least inconsistent to regard decompositions of this kind taking place at high temperatures in a light different from quite analogous decompositions taking place at a lower temperature, and, in fact, to consider the former as abnormal, and to try by various artifices to explain them away. The fact to be recognised is that chemical changes requiring for their completion the aid of heat can take place under various conditions, and that such changes do take place more frequently, and the more easily the more heat there is to be disposed of, consequently at higher temperatures, but that such changes do not take place exclusively at high temperatures."

Decompositions associated with negative calorific effects take place usually very easily in association with others producing heat, so that in the total effect more heat is produced than is used. This may be well illustrated by a series of reactions on which an important metallurgical process (Claudet's) depends. Zinc iodide is used to separate silver from silver chloride, dissolved in brine, the equation being



The separation of chlorine from silver by the iodine of iodide of zinc is quite in accordance with the fact that a greater amount of heat is liberated by the formation of chloride of zinc than silver chloride. In the second stage of the process, zinc again takes the iodine from iodide of silver, the heat of formation of zinc iodide being greater than that of silver iodide.



It is well to repeat that in the following equations the figures representing the thermal values are preceded by the plus or minus sign. This is a conventional mode of representation of the fact that heat has been gained or lost during the formation of the particular compound. In calculating the thermal value of

<sup>1</sup> *Modern Theories of Chemistry*, p. 442.



any given set of reactions as represented by an equation, it is necessary to algebraically subtract the thermal value of all compounds that are decomposed, and, conversely, to algebraically add the thermal values of the bodies formed.

The elements are assumed to be in the normal state of aggregation unless it be otherwise stated, so that although an equation may be written  $\text{CuS} + 3\text{O} = \text{CuO} + \text{SO}_2$ , it must be understood that it is oxygen in its normal condition that is employed, and not nascent oxygen. The heats of aggregation are only known in a very few instances.

The heats of formation given in the following tables are mainly derived from the results found in the *Annuaire du Bureau des Longitudes*. The numbers therein given have been adapted to agree with the chemical notation in use in this country. They are, it is believed, the most trustworthy that can be set before the student, and with their aid he will be able to obtain an insight into the thermal conditions which prevail when some of the

#### HEATS OF FORMATION OF SOME GASEOUS COMPOUNDS.

Reaction.	Product.	Heat Evolved.	State of Product.
S + 3O	SO <sub>3</sub>	+ 91.8	Gaseous.
"  "	SO <sub>3</sub>	+ 103.6	Solid.
S + 2O	SO <sub>2</sub>	+ 71.0	Gaseous.
2H + O	H <sub>2</sub> O	+ 58.2	"
"  "	H <sub>2</sub> O	+ 69.0	Liquid.
C + 2O	CO <sub>2</sub>	+ 97.0	Gaseous.
C + O	CO	+ 29.0	"
2H + S	SH <sub>2</sub>	+ 4.6	"

principal metallurgical operations are being conducted. The thermal equations given on page 397 will provide the student with a basis for such work. It will be observed that the synopsis of typical processes, page 405, contains reference numbers to these sets of distinctive thermal processes. It must, at the same time, be admitted that the basis for thermo-metallurgy is at present a somewhat slender one, as most of the data which have as yet been obtained are derived from "wet," and not "dry" reactions. It is well, therefore, to bear in mind the warning of Mendeléeff against "extracting exact consequences of importance to chemical mechanics" from the present store of thermo-chemical data. He points out<sup>1</sup> "that the majority of the determinations were conducted in weak aqueous solutions, and, the heat of the solution being known, were referred to the substances in solution." It must be remembered, however, it is probable that during both

<sup>1</sup> *The Principles of Chemistry*, vol. i., 1891.



solution and dilution the water acts independently in a chemical sense on the substance dissolved, and that "physical and mechanical changes proceed side by side with chemical changes . . . . and for the present it is impossible to distinguish the thermal effects of the one and of the other kind of change . . . purely chemical phenomena are inseparable from mechanical phenomena."

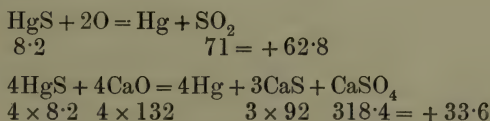
### HEATS OF CHANGE OF THE ISOMERIC ELEMENTS.

Name.	Heat Evolved.
Oxygen, changing to ozone (16 grammes) . .	- 9.9
Sulphur, octahedral to insoluble variety . .	0.0 at 18° < 0 at 112°
„ insoluble amorphous to the soluble amorphous variety . . . .	+ 0.08
„ soluble amorphous to the octahedral . .	- 0.08
„ prismatic to octahedral . . . .	+ 0.08
„ plastic to octahedral . . . .	+ 0.40
Selenium, vitreous to metallic variety . .	+ 5.6
Tellurium, crystalline to amorphous variety .	+ 24.2
Phosphorus, white to red crystalline „ .	+ 19.2
„ „ „ amorphous „ . .	+ 20.7 + 9.3 and - 1.0, according to the modification.
Arsenic, amorphous to crystalline variety . .	+ 1.1
Carbon, amorphous (charcoal) to diamond . .	+ 3.4
Silicon, amorphous to crystalline variety . .	+ 8.1
Gold, precipitated from the bromide, to the physical state of gold precipitated from the chloride . . . . .	+ 3.2
Iron, about 650° . . . . .	- 0.28
„ „ 850° . . . . .	- 0.34

### THERMAL EQUATIONS FOR THE PRINCIPAL METALLURGICAL OPERATIONS.

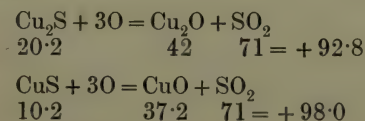
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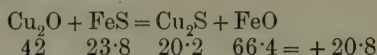
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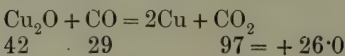
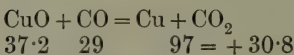
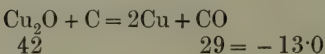
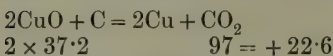
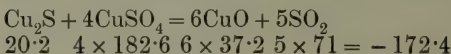
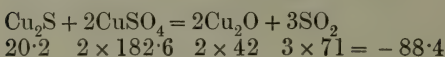
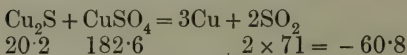
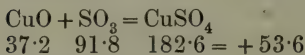
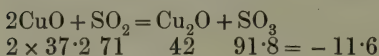
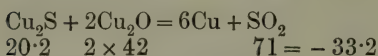
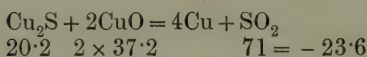
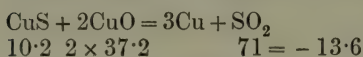
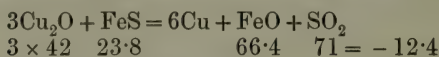
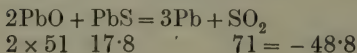
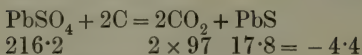
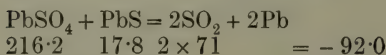
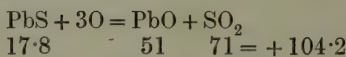
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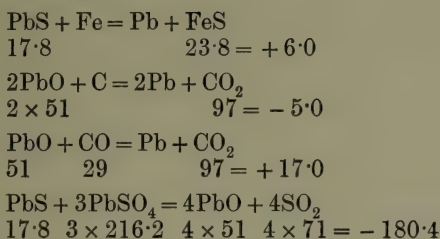
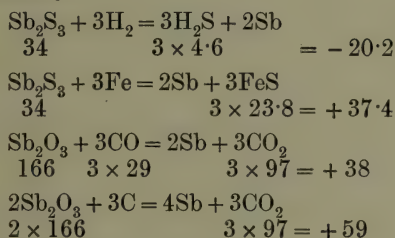
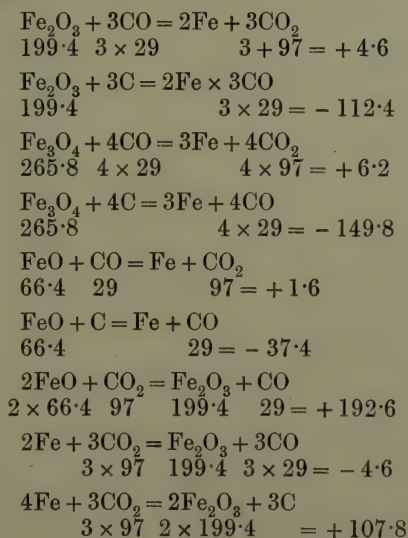
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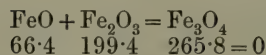
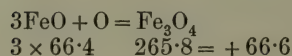
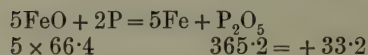
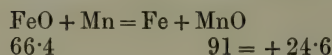
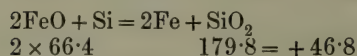
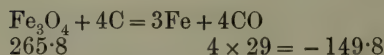
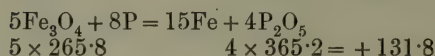
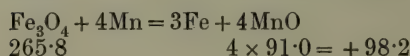
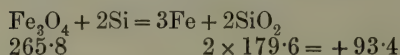
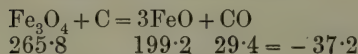
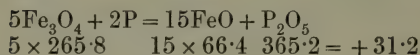
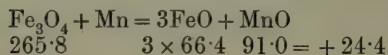
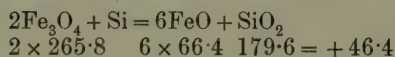
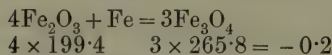
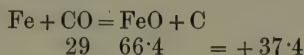
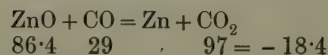
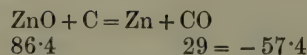


**Copper**—*continued*.

When heated in presence of silica,  $\text{Fe}_2\text{SiO}_4$  is formed

**III.****Lead.**

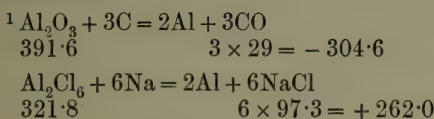
**Lead**—*continued*.**IV.****Antimony.****V.****Iron.**

**Iron**—*continued*.**VI.****Zinc.**



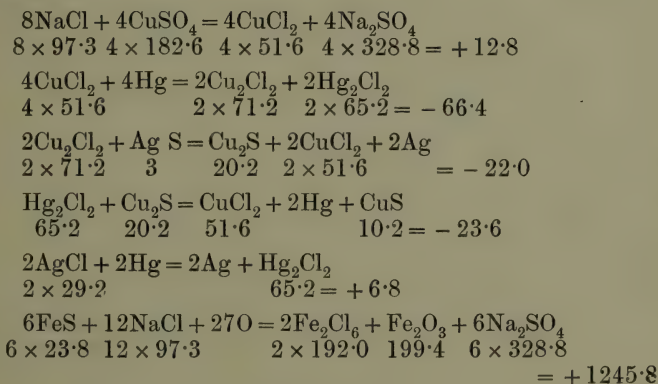
## VII.

## Aluminium.



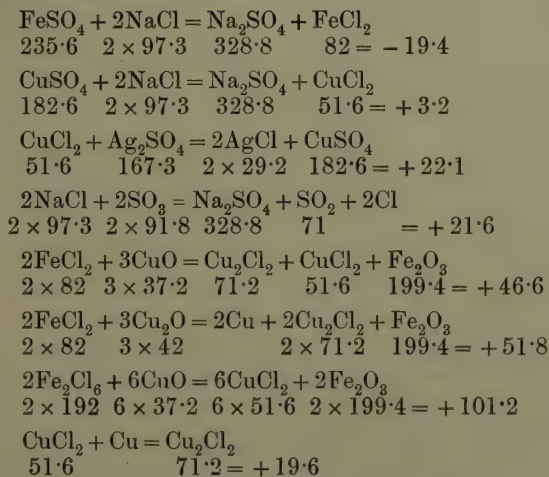
## VIII.

## Silver.



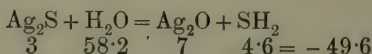
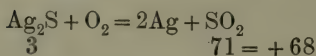
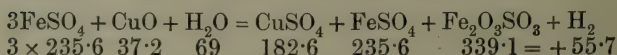
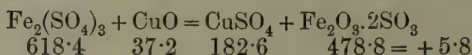
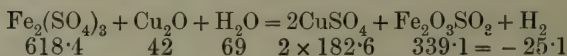
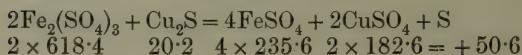
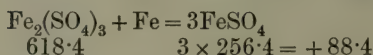
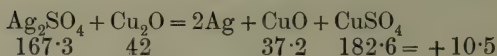
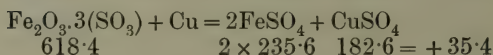
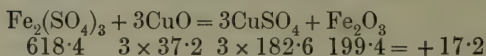
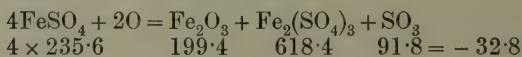
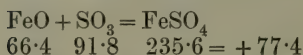
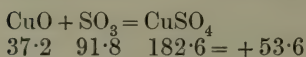
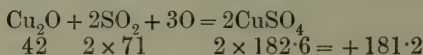
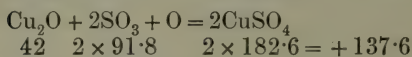
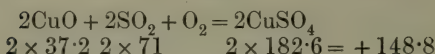
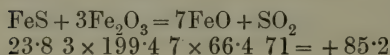
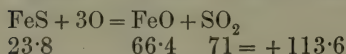
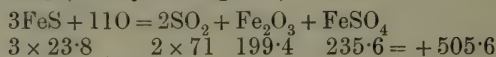
## IX.

## Chloridising Roasting.

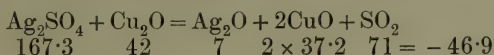
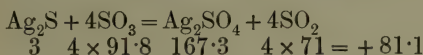
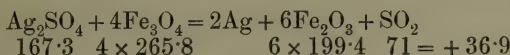
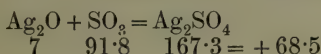
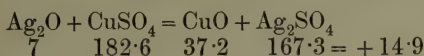
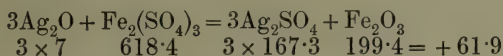
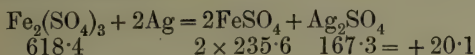
<sup>1</sup> Fremy, *Encyclopédie Chimique*, Paris, 1890.

## X.

## Roasting (mainly to Sulphate).

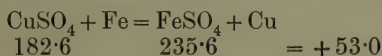
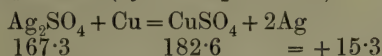


## Roasting—continued.



## XI.

## Precipitation (by a cheaper metal).



See also III. and IV. for cases of precipitation in the dry way of lead and antimony, from their sulphides, by iron.

The table given on the folding plate will enable the student to form other thermal equations for himself.

In calculating the heats of formation of the basic ferric sulphates, it has been necessary to assume that the heat evolved is proportional to the ratio of acid to base. It must be remembered that in the case of the combination of carbon and oxygen such a relationship does not exist.

## BIBLIOGRAPHY.

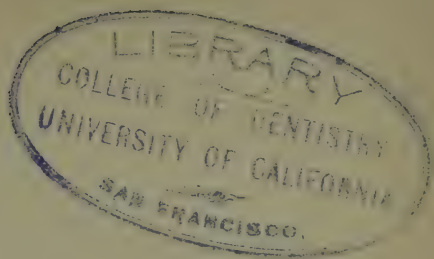
- Berthelot.—*Essai de Mécanique Chimique* (Paris, 1879); *Traité Pratique de Calorimétrie Chimique* (Paris).  
H. Le Chatelier.—*Equilibres Chimique* (see Comptes Rendus, vol. cvi., 1888, pp. 355, 598, 1008).  
Prof. A. Ditte.—*Leçons sur les Métaux* (Paris, 1891).  
P. Duhem.—*Introduction à la Mécanique Chimique* (Paris, 1893).  
J. Willard Gibbs.—*On the Equilibrium of Heterogeneous Substances* (Trans. Connecticut Acad., vol. iii.).

- J. Moutier.—*Sur quelques relations de la Physique et de la Chimie* (Ency. Chimique de Fremy, Introduction, 1881).
- Pattison Muir.—*The Elements of Thermal Chemistry* (London, Macmillan, 1885).
- Muir and Wilson.—*Principles of Thermal Chemistry* (London, 1885).
- A. Naumann.—*Technisch-thermochemische Berechnung zur Heizung insbesondere mit gas-förmigen Brennstoffen* (Braunschweig).
- W. Nernst.—*Theoretische Chemie* (Stuttgart, 1893).
- Ostwald.—*Lehrbuch der allgemeinen Chemie* (Leipzig, 1893).
- J. Thomsen.—*Thermochemische Untersuchungen* (Leipzig, 1882-3). English translation by K. A. Burke, B.Sc. (London, Longmans, Green & Co.).
- J. J. Thomson.—*On the Application of Dynamics to Physics and to Chemistry* (London, Macmillan, 1888).



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## CHAPTER XII.

### TYPICAL METALLURGICAL PROCESSES.

**Classification of Processes.**—The methods that are adopted in extracting metals from their ores may conveniently be grouped in the following manner :—

The thick, black Roman numerals refer to the Thermal Equations,  
Chapter XI.

#### A. DRY PROCESSES.

##### I. *a. By Simple Fusion with Suitable Fluxes.*

(a) In blast or reverberatory furnaces.	1. Gold . . .	} This process is only applicable to metals in an uncombined form.
	2. Silver . . .	
	3. Platinum . . .	
	4. Copper . . .	
(b) In tube-furnace.	5. Bismuth . . .	By liquation.

##### *β. By Simple Heating.*

(a) In kilns or reverberatories.	1. Mercury (I.) . . .	From its sulphide, the presence of air being necessary.
(b) In retorts.	2. Arsenic . . .	From sulphides of arsenic and iron, air excluded, always with appliances for condensing the volatilised metal.

#### II. *By Reduction of Oxide by Carbon.*

(a) In blast-furnaces or, more rarely, in hearths or crucibles.	1. Copper (II.) . . .	} Usually after previous roasting of sulphide or arsenide ;
	2. Lead (III.) . . .	
	3. Antimony (IV.) . . .	
	4. Nickel . . .	} Usually with simultaneous carburisation of the liberated metal.
	5. Iron (V.) . . .	
(b) In reverberatory furnace.	6. Nickel . . .	
	7. Manganese . . .	
	8. Tin . . .	
	9. Bismuth . . .	

- |                                      |                             |  |
|--------------------------------------|-----------------------------|--|
| (c) In retort-furnaces.              | 10. Zinc (VI.) . . .        | $\left\{ \begin{array}{l} \text{Always after roasting the} \\ \text{ore; and with volatilisa-} \\ \text{tion of the liberated metal.} \end{array} \right.$ |
|                                      | 11. Arsenic . . .           |  |
|                                      | 12. Sodium . . .            |  |
| (d) In furnaces heated electrically. | 13. Aluminium (VII.)        |  |
|                                      | 14. Calcium, chromium, etc. |  |

### III. *By Concentration as Sulphide;*

usually followed by reaction between sulphide and oxide,  
or between sulphide and sulphate.

- |                                |                 |  |
|--------------------------------|-----------------|--|
| (a) In reverberatory furnaces. | 1. Copper (II.) | $\left\{ \begin{array}{l} \text{Usually after partial roasting;} \\ \text{sometimes, in the case of lead and} \\ \text{antimony, the removal of the} \\ \text{sulphur and precipitation of the} \\ \text{metals is aided by a cheaper} \\ \text{metal, iron.} \end{array} \right.$ |
| (b) In liquation-furnace.      | 2. Lead (III.)  |  |
|                                | 3. Antimony     |  |
| (c) In Bessemer converter.     | 4. Copper.      |  |

### IV. *By Concentration in Sulphide, or Arsenide,*

and subsequent smelting as in II. or III.

- |                                     |            |
|-------------------------------------|------------|
| In reverberatory or blast-furnaces. | 1. Gold.   |
|                                     | 2. Silver. |
|                                     | 3. Copper. |
|                                     | 4. Nickel. |
|                                     | 5. Cobalt. |

### V. *By Concentration in Other Metals, by Fusion.*

- |   |              |  |
|---|--------------|--|
| Usually in blast-furnaces, but often in reverberatory furnaces. | 1. Gold.     | The metal is subsequently concentrated or extracted by (1) cupellation, (2) crystallisation (Pattinson process), (3) liquation, (4) recourse to wet methods, (5) superior affinity of a third metal (zinc in Parkes' process), (6) electrolysis. |
|   | 2. Silver.   |  |
|   | 3. Platinum. |  |

### VI. *By Reduction of a Haloid Salt.*

- |  |               |   |
|--|---------------|---|
| In reverberatory furnaces or in crucibles. | 1. Aluminium. | $\left\{ \begin{array}{l} \text{The halogen is removed by} \\ \text{sodium.} \end{array} \right.$ |
|  | 2. Magnesium. |   |

## B. PROCESSES INVOLVING THE USE OF MERCURY.

- |  |   |   |
|--|---|---|
| (a) In cradles, flumes, stamp batteries, concentrators . . . | $\left. \begin{array}{l} 1. \text{ Gold} \\ 2. \text{ Silver (VIII.)} \end{array} \right\}$ | $\left\{ \begin{array}{l} \text{As part of the operation} \\ \text{of dressing the ore.} \end{array} \right.$   |
| (b) In pans and appliances of varied form . . .              |   |   |
| (a) In heaps . . .   | $\left. \begin{array}{l} 2. \text{ Silver (VIII.)} \end{array} \right\}$                    | $\left\{ \begin{array}{l} \text{Patio process.} \\ \text{Old Freiberg process.} \\ \text{Cazo process.} \\ \text{Modern pan-amalgamation.} \end{array} \right.$ |
| (b) In barrels . . .   |   |   |
| (c) In copper-lined tubs . . .                               |   |   |
| (d) In cast-iron pans . . .                                  |   |   |



## C. WET PROCESSES.

*a. Methods of Solution.*

These processes are usually conducted in earthenware vessels, cast-iron pans, or vats, usually lined.

I. *a. Solution in Acids.*

- |                   |  |
|-------------------|--|
| 1. Gold . . .     | In aqua regia.   |
| 2. Platinum . . . | " "  |
| 3. Silver . . .   | In nitric or sulphuric acid.   |
| 4. Bismuth . . .  | In hydrochloric acid.  |
| 5. Nickel . . .   | The oxides, obtained by roasting sulphides<br>or arsenides, are dissolved usually in hydro-<br>chloric acid. |
| 6. Cobalt . . .   |  |
| 7. Zinc . . .     |  |
| 8. Copper . . .   |  |
| 9. Lead . . .     |  |

*b. Solution in Alkaline Salts.*

- |                 |                       |
|-----------------|-----------------------|
| 1. Gold . . .   | In potassium cyanide. |
| 2. Silver . . . | " "                   |
| 3. " . . .      | In hyposulphites.     |

II. *Roasting to Sulphate, and extracting with Water.*

- |                       |                                    |
|-----------------------|------------------------------------|
| 1. Silver (X.) . . .  | (Ziervogel process.)               |
| 2. Copper (II.) . . . | The metal is precipitated by iron. |

III. *Roasting with Salt, Soluble Chloride being formed.*

- |                       |                                      |
|-----------------------|--------------------------------------|
| 1. Silver (IX.) . . . | (Augustin and Von Patera processes.) |
| 2. Copper . . .       | (Longmaid and other processes.)      |

IV. *Formation of Soluble Chloride by Gaseous Chlorine.*

- |                 |   |
|-----------------|---|
| 1. Gold . . .   | Plattner's process and its modifications.<br>Or bromine may be used, a soluble bromide<br>being formed.             |
| 2. Silver . . . | Any silver chloride, formed in the treat-<br>ment of gold, may be dissolved out by<br>sodium hyposulphite or brine. |

*β. Methods of Precipitation.*

- |                       |  |
|-----------------------|--|
| 1. Silver . . .       | Replacement by a cheaper metal.<br>By a precipitating agent.<br>By a reducing gas. |
| 2. Copper (XI.) . . . |  |
| 1. Gold . . .         |  |
| 2. Platinum . . .     | By precipitation, followed by reduction in<br>the dry way.                         |
| 1. Bismuth . . .      |  |
| 2. Nickel . . .       |  |
| 3. Cobalt . . .       |  |
| 4. Zinc . . .         |  |
| 5. Lead . . .         |  |

## D. ELECTROLYTIC METHODS.

At the present time, electrolysis is mainly employed in the refining of copper,<sup>1</sup> less so in gold and silver refining,<sup>2</sup> in the precipitation of gold from dilute solutions,<sup>3</sup> and in the treatment of argentiferous lead. Numerous electrolytic methods of extracting and refining metals from their ores have been brought forward; few, however, have advanced beyond the experimental stage, of which the following are examples:—

1. Copper . . . From blister-copper or regulus.
2. Lead . . . Bett's process.
3. Gold . . . By nascent chlorine produced electrolytically.
4. Aluminium . . From aluminium in its fused salts.
5. Antimony . . Borchers' process.<sup>4</sup>
6. Zinc . . . Electrolytic wet or dry methods.
7. Steel . . . Various methods, some already described.

Full descriptions of the methods adopted in extracting even the principal metals from their ores are not needed here, as the student has an abundant technical literature at his disposal. It is far more important for the student to become familiar with the nature of metallurgical operations generally, so that he may see how they differ from those conducted either in the laboratory or in purely chemical works. Hence a few typical metallurgical processes with considerable complexity of detail have been chosen for somewhat full treatment, since a knowledge of such groups of processes as those adopted at Swansea, Denver, and Freiberg gives the student a clearer insight into the practice of metallurgy than desultory reading affords.

**Welsh Method of Copper-smelting.**—This method, in modified forms, conducted in reverberatory furnaces, was until recently employed for a large proportion of the world's production of copper. In Germany a blast-furnace method is employed for the earlier stages. The one broad distinction between this method and the Welsh method consists in the fact that in the latter copper sulphide is the reducing agent, whilst in the German process it is carbonic oxide. Both processes depend essentially on the affinity which copper has for sulphur, which enables it to form a regulus while the associated metals are eliminated in an oxidised form.

In the Welsh method (fig. 183) comparatively poor ores, consisting of copper pyrites with a considerable proportion of iron pyrites, containing 5 to 15 per cent. of copper, richer ores of the same composition containing 15 to 25 per cent. of copper, and

<sup>1</sup> Peters, *Copper Smelting*, p. 576; *Mineral Industries*, vol. vii. (1899), p. 229.

<sup>2</sup> Rose, *Metallurgy of Gold*.

<sup>3</sup> *Ibid.*

<sup>4</sup> *Dingler's Polytechnisches Journal*, vol. cclxvi. (1887), p. 283. On electrolytic methods consult Balling, *Die Electro-Metallurgie*.



copper, and 18 to 22 per cent. of sulphur, and *metal-slag*, which is a ferrous silicate, containing a little oxide of copper and shots of metallic copper, the total amount of copper it contains being 2 to 3 per cent. This slag is melted in operation 2.

5. *Roasting the Regulus*.—This operation is very complex, and comprises a series of roastings and fusion in an oxidising atmosphere. Its object is to purify the regulus and to scorify the iron, and to bring as much as possible of the copper to the metallic state. To operations of this character the Welsh smelter applies the term *roasting*, as distinguished from *calcining*. Two products are obtained, *blister-copper*, containing about 98 per cent. of copper, and a slag, *roaster-slag*, which always contains oxide of copper, shots of metallic copper, and often a small proportion of arsenic, antimony, and tin. This slag is usually added to the charge in operation 4.

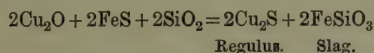
6. *Refining and Toughening*.—The object of this operation is to purify the copper by oxidising the foreign bodies that it contains. The refining should bring the metal to the malleable state of *marketable* copper. The slag obtained, *refinery-slag*, is very rich in copper, about 55 per cent., and is added to the charge in operation 4.

In the original Welsh method of copper-smelting, reverberatory furnaces were exclusively employed, the area of the grate being generally about one-fifth of that of the hearth. The tendency, however, has been of late years to reduce the number of operations by judiciously mixing burnt pyritic ore with oxidised ores and slag, and running to a regulus in small cupolas or blast-furnaces. Subsequent enrichment of the regulus, reduction, and refining are still conducted in reverberatory furnaces. The ore is charged-in through a flat hopper, in which it is allowed to dry for some time before being introduced into the furnace. The internal dimensions of the calcining-furnaces are usually 30 feet by 12 feet, or 21 feet by 12 feet. The charge is 3 to 6 tons of ore, the calcination occupying twelve to twenty-four hours. The doors are then closed, and the temperature raised in order to decompose the sulphates. The gas evolved may consist of 10·6 per cent. of sulphurous and carbonic anhydrides, 9 per cent. of oxygen, and 80 per cent. of nitrogen.

The reverberatory furnaces, in which the fusion for regulus is effected, are so arranged as to give a high temperature, and the fireplace is consequently large in comparison with the laboratory portion. The bed consists of a series of layers of compressed sand cemented with metal-slag. It is about 15 to 20 inches in thickness, and slopes in all directions towards a tap-hole. There is a door in proximity to the flue, and through this door the slag is skimmed without allowing the air to pass over the regulus and oxidise it. In front of the tap-hole is a perforated receptacle, which can be lowered by a crane into a tank full of water. The bed is about



14 feet long, the distance between the top of the bridge and the roof being 23 inches. The charge is usually 2 tons of ore. Slags from subsequent operations are added, and fluorspar, if much earthy gangue is present. The materials used in the first fusion for regulus are chiefly oxides and sulphides of copper and iron, and the operation consists essentially in obtaining copper sulphide, thus :—

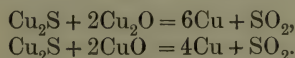


The sulphides must be in excess, otherwise copper will be reduced and oxide of copper formed which will pass into the slag.

The calcination<sup>1</sup> of the regulus is effected in a furnace similar to that used for the first calcination. The charge is  $3\frac{1}{2}$  to  $6\frac{1}{2}$  tons of regulus. The reactions taking place are similar to those in the first calcination. The process occupies twenty to thirty-six hours, and 12 per cent. of the sulphur is eliminated.

The second fusion is conducted in a similar manner to the first fusion for coarse-metal. The charge is 2 tons of calcined coarse-metal and 12 cwt. of slag and oxidised ores. The regulus obtained consists of white-metal (75 per cent. of copper), or blue-metal (60 per cent. of copper), or pimple-metal (81 per cent. of copper). The slag is a silicate of iron, with about 4 per cent. of copper. The reactions are similar to those that obtain in the first fusion for regulus. Blue-metal contains some sulphide of iron, and pimple-metal contains an excess of the oxidised copper compounds. When very impure ores are dealt with, it is often found advisable to allow a little coarse copper to form as bottoms.

The roasting of these different varieties of regulus is conducted in a reverberatory furnace with a deep hearth. The process is prolonged as much as possible, and thus the arsenic and antimony may be caused to escape before the actual reducing action commences. When the pasty mass has collected at the bottom of the furnace the temperature is raised, and the reaction between the sulphide and the oxide takes place, metallic copper being formed. The chief reactions may be expressed thus :—



This impure copper, blister-copper, is refined in furnaces similar to those used for fusion, except that the bed is deeper and the fireplace larger. The charge consists of about 10 tons of blister-copper in the form of pigs, which are loosely stacked, and an abundant supply of air is provided, so as to oxidise the metal as much as possible. The temperature is raised gently to the melting-point of copper; it is then moderated in order that the fusion

<sup>1</sup> Copper-smelters call these operations *calcination*, but *roasting* would be more accurate.

may be prolonged and oxidation occur. The melting occupies five to six hours, and the moderate heating is continued for five to six hours more, in order that the iron, antimony, arsenic, etc., may be completely oxidised. The temperature is then raised much higher for three to four hours more, when the oxidised products form a thin slag, containing a considerable quantity of copper oxide. This is raked off, and the surface covered with a layer of the purest anthracite or charcoal. A long pole of wood, green wood by preference, is pushed beneath the surface of the molten metal and held down by a suitable metal bar. The violent evolution of gas from the wood causes the metal to splash up amongst the carbonaceous covering, and this, with the gases from the wood, reduces, to the metallic state, the copper oxide that exists dissolved in the copper to the extent of 4 per cent. A small amount of the oxide must be left, and the workman judges, from a sample that he takes from time to time and tests by breaking in a vice, whether it is still "underpoled" or at "tough-pitch," that is, ready for market, or "overpoled." If the last, he removes the carbon covering, and exposes the metal to the action of the air.<sup>1</sup>

In the so-called "direct" process, first successfully carried out at the Cape Copper Works, one portion of the rich regulus is carefully roasted in revolving cylinders or automatic rake calciners. This is then mixed with the unroasted portion and smelted in reverberatory furnaces, the above equations representing the changes. The feature of this method is that refined copper is produced in the one furnace and not the intermediate product, blister-copper. The original Welsh process has now undergone such modification that very little difference exists between it and the methods adopted in Germany at the well-equipped smelters of the Mansfeld Gewerkschaft, and also those of Freiberg and in the Harz mountains. In many of the modern works<sup>2</sup> in the United States the reverberatory furnace has been entirely dispensed with, and the process adopted consists in blast-furnace smelting for a regulus which is conveyed in the molten state to Bessemer converters. Here air is blown through the molten regulus, and copper is reduced to the metallic state, the reactions taking place being practically the same as those that

<sup>1</sup> Fuller information on the Welsh method of copper-smelting will be found in the following works:—

Percy, *Metallurgy*, vol. i. (London, 1861), p. 314.

Vivian, *Copper Smelting: Its History and Processes*, 1881.

Howe, *Copper Smelting*, Washington, 1885.

Le Play, *Procédés Métallurgiques employés dans le Pays de Galles*, Paris, 1848.

Rivot, *Principes généraux du Traitement des Minéraux métalliques*, Paris, 1871.

Peters, *Copper Smelting*, and also *The Principles of Copper Smelting*.

<sup>2</sup> Peters, *Copper Smelting*.

take place during reduction in reverberatory furnaces. The copper reduced in the converters is cast direct into anode plates and passed on to the electrolytic refineries.

**Smelting of Gold and Silver Ores in Colorado.**—The following is a short sketch, borrowed from Mr R. Pearce's Presidential Address, delivered at the meeting of the American Institute of Mining Engineers, in June 1889, of the methods formerly used at the Boston and Colorado Smelting Works. These methods, however, have now been replaced by more modern processes.

About 200 tons of ore are smelted per day, the ores including a great variety of copper, silver, and gold ores from Colorado, as well as from other Western States and Territories, and averaging 40 to 60 oz. of silver and  $\frac{1}{2}$  to 1 oz. of gold per ton, and 2 to 3 per cent. of copper. About 90 per cent. of the ore contains no copper, the other 10 per cent. furnishing that metal in sufficient quantity to make up the general average to 2 to 3 per cent. Half the ore, 100 tons per day, is roasted in furnaces or in kilns, but the operation is not complete in either case, as sulphur is always allowed to remain to the extent of 5 to 7 per cent. The other 100 tons are smelted without roasting. The roasted ore and siliceous ores are mixed so as to yield a slag containing 40 per cent. of silica and a regulus (ore metal) containing 40 per cent. of copper and 400 oz. of silver and 6 oz. of gold per ton. The capacity of each furnace is about 25 tons of ore per day, with 2 tons of rich slag added from other operations. In this smelting 13 tons charged yield 1 ton of ore-metal. This regulus always contains a certain amount of lead, but the proportion rarely exceeds 10 per cent.

In the next stage of the process, the charge consists of a mixture of two-thirds of roasted ore-metal and one-third of unroasted ore-metal, together with the rich siliceous silver ore, in quantities sufficient to prevent corrosion of the furnace by the iron in the regulus. The concentration-furnace in which this operation is effected stands 3 feet above the level of the ore-furnace, so that the rich slag from the former may, when skimmed, flow directly into the latter, where it is reduced to the condition of ordinary ore-furnace slag. This effects a great saving in the cost of re-smelting these rich slags. The regulus obtained contains 700 to 800 oz. of silver and 10 oz. of gold per ton, together with 60 per cent. of copper, each ton representing 20 to 21 tons of ore. This regulus is now ready for the extraction of the silver, which comprises the following operations:—

Rough roasting.

Fine grinding.

Fine roasting for silver sulphate.

Lixiviation, and the precipitation of the silver.

Refining and melting of the cement silver.

The regulus is crushed so as to pass through a screen of 6



meshes to the inch, and roasted for twenty-four hours. The bulk of the sulphur is driven off, and oxide of copper is formed, the mass still containing sufficient sulphur for the subsequent operation of roasting for silver sulphate. After cooling, the roasted material is ground finer under edge-rollers and passed through a 60-mesh screen. It is then ready for fine roasting or conversion of the sulphide into sulphate.

This operation, based on principles pointed out by Ziervogel, lasts about five hours. The first stage is conducted at a low temperature, and lasts about an hour and a half, copper sulphide being oxidised with evolution of heat. In the second stage, at a slightly increased temperature for an hour and a half, the material increases in volume, and assumes a porous appearance from the formation of copper sulphate. In the third stage, the temperature is further increased for an hour, or until the silver is completely changed into sulphate. If cuprous oxide is present at this stage, it will, during the operation of lixiviation with water, cause the reduction of the silver sulphate to metallic silver. The charge is consequently vigorously stirred, and turned over, in the fourth and last stage, in order completely to oxidise any cuprous oxide. The results of the operation are very materially affected by arsenic, by antimony, and, above all, by bismuth, metals which form insoluble silver compounds. The lixiviation of the roasted regulus is effected in tubs, and nothing but hot water is required. The solution, charged with silver sulphate, is allowed to flow over copper plates for the precipitation of the silver, a process requiring but little attention. The solution enters tank No. 1, charged with silver, and leaves tank No. 2, charged with copper, and without a trace of silver. It finally flows over scrap-iron for the precipitation of the copper. In the precipitated silver, some copper is found in the form of cuprous oxide or as metal. This is removed by prolonged boiling with water containing a small quantity of sulphuric acid, into which air is injected by a small steam-jet. The copper sulphate formed is carefully washed out of the silver, which is then dried and melted into bars of an average fineness of 999.

The residues from the silver extraction contain about 40 oz. of silver and 10 oz. of gold per ton, and 65 per cent. of copper as cupric oxide. They also contain lead and bismuth as sulphates, and iron as ferric oxide. They are mixed with pyritic ores containing gold, pyrites rich in sulphur, and siliceous gold ores, and are smelted direct for regulus with 65 per cent. of copper, and 10 to 15 oz. of gold and 80 oz. of silver per ton. The slag, which is similar in composition to that from the ore-furnace, is thrown away.

This regulus is treated so as to obtain a rich copper-gold alloy. This process involves two operations—(1) a combined roasting and smelting, and (2) a refining of the crude alloy. The aim of the



process is to concentrate the gold contained in the regulus into a rich gold-silver-copper alloy, containing also the bulk of the impurities existing in the regulus. This process is similar to the Swansea method of making "best selected copper." At Argo, about 12 tons of slabs of regulus, residue metal, are placed on the hearth of a large reverberatory furnace, and melted after partial oxidation. In the last stage of the melting, a reaction takes place between the oxide and sulphide, and a certain amount of metallic copper is liberated. This contains nearly all the gold, together with any foreign metals present in the regulus. The charge is tapped into sand-moulds, and the first few pigs nearest the tap-hole are found to have, under the enriched regulus, plates of this impure copper, commonly known as metallic bottoms. The proportion of these to the whole tap of regulus, or pimple-metal, is about 1 to 15. The bottoms contain 100 to 200 oz. of gold to the ton, and about 300 oz. of silver. They are subjected to processes of refining and separation, whereby the gold is recovered.

The pimple-metal, if the operation has been properly conducted, contains 0.1 to 0.2 oz. of gold per ton, 90 oz. of silver, and 77 per cent. of copper. It is crushed, roasted, ground fine, and again roasted to form silver sulphate. In fact, it is treated by the Ziersch process in precisely the same manner as the rich silver regulus; but, as it contains little gold, a separate set of furnaces is used. The residue consists almost entirely of copper oxide with less than 10 oz. of silver per ton. It is dried, packed in barrels, and sold to the manufacturers of sulphate of copper, or is reduced to black copper by melting with small coal slack in a reverberatory furnace.

Thus it will be seen from the above brief sketch how intimately associated are the modern methods of metallurgy as applied to gold, silver, copper, and lead. For a full description of these methods the students should refer to the other volumes of this series.<sup>1</sup>

In these volumes detailed descriptions are given of the modern methods of treating complex ores containing the four above-mentioned metals in quantities sufficient to render their extraction profitable. It will be seen to what a high state of efficiency the processes have been carried; how by judicious dressing the sulphides and oxidised material are carefully separated and subjected to special treatment, in the case of silver ores by the modifications of the original amalgamation processes and the newer "wet" processes. In these, stress is laid on the operation of roasting, this being regarded as the crucial point upon which the commercial success of the process may depend. Consequently the object of dressing methods is to limit the amount of material requiring this treatment, and to effect the operation by appliances which shall give a high efficiency.

<sup>1</sup> Collins, *Metallurgy of Lead and Silver*.

**Freiberg Process.**—The smelting works at Freiberg,<sup>1</sup> in Saxony, were originally established to treat the ores obtained from the mines of the district. At the present time, ores from all parts of the world are also smelted. There are also two works, of which the more important (the Halsbrüche Hütte) is situated about three miles from the town of Freiberg, the other (the Muldenhütte) being somewhat more distant.

The ores treated consist chiefly of the sulphides of lead; but silver and copper are always present in the mixture of ores which constitutes the furnace-charge. The plant also includes furnaces for the treatment of ores of zinc, arsenic and antimony fume. As an incidental process, sulphuric acid is made both by the ordinary lead-chamber method, and by a process in which the gases containing the sulphurous anhydride are stated to be passed over perforated clay slabs covered with platinised asbestos. Bismuth is also extracted from the portions of the cupellation-hearths in which is collected the greater part of the bismuth that was originally contained in the lead treated. Provision is also made for the extraction of copper, nickel, and cobalt present in the ores. The various departments of the work are kept distinct, and the treatment, as a whole, centres round the smelting of the lead ores, the various residues from the treatment of other ores, frequently rich in the precious metals, being added to the lead-smelting charge. It is in this latter treatment that the distinctive features of the Freiberg smelting process are found, the lead ores being smelted in admixture with the copper ores and argentiferous and auriferous residues. For this purpose the Pilz water-jacketed furnaces are used. They were originally introduced about the year 1865 to replace the older types of blast-furnace which had long been employed. The extraction of silver by the classical Freiberg amalgamation process, conducted in barrels, was also abandoned about this period, and was replaced by the method still in use, by which the precious metals are collected in the smelted lead. The main features of this process are as follows:—In order to impart the necessary degree of strength and coherence to enable them to be treated in the blast-furnace, as well as to obtain them in pieces of a size adapted to such treatment, the ores are first roasted at a temperature sufficiently high to clot the mass. This is effected by subjecting a suitable mixture of ores to an oxidising roasting in a long-bedded reverberatory furnace. The sulphur of the ore is in this way oxidised, and the metals are left chiefly in the form of oxides. Towards the end of the roasting the temperature of the furnace is raised to a degree sufficient to partly fuse the oxidised charge then present; the roasted material can in this state be withdrawn from the furnace into sheet-iron wheel-barrows, in which it is allowed to solidify. The

<sup>1</sup> The description of this process has been left practically in its original form, as it includes several typical metallurgical operations.

solidified material is afterwards broken up into pieces of the desired size, and classified according to the completeness with which the roasting has been effected, as indicated by the presence or absence of unroasted sulphide. It is then smelted down in the Pilz furnaces, in admixture with coke and brown coal. The products of this smelting are (1) lead; (2) a regulus, or mixture of fused sulphides of lead and copper; (3) a slag; and (4) a lead fume. A small quantity of speise, containing nickel and cobalt, is also occasionally obtained. The lead produced contains the greater part of the precious metals originally present in the charge, together with some copper and other impurities. Such lead has always to be subjected to a refining process before being desilverised by the method in use at the works, and, if very impure, a secondary refining process of liquation has also to be used. To avoid the necessity of this, the charge is usually maintained as free from impurities as possible, the percentage of the copper being at the same time kept low. The slag from the ore-smelting always contains lead in too large a quantity to admit of its being thrown away. It has therefore to be re-treated, and, as the lead obtained from this source is always very impure, any impure materials that it may be necessary to deal with are generally treated simultaneously with the slag, provided they are not too rich in the precious metals. The percentage of copper admissible in the furnace-charge for this slag-smelting is also greater than in that for the treatment of the ore. The ore-slag is treated in admixture with materials poor in silver and in lead, in a manner similar to the method adopted when smelting the ore. The products are the same as before—lead, speise, regulus, slag, and fume. The lead, however, is much less in relative quantity, and more impure than that obtained from the ore-smelting; speise is a more frequent product, the regulus obtained is richer in copper, and the slag is so poor in silver and lead that it may be thrown away.

The further treatment of these various products is as follows:—

*Lead.*—The slag-lead, and occasionally the ore-lead, is first submitted to a liquation process, which consists in melting the lead at as low a temperature as possible, on the sloping bed of an ordinary reverberatory furnace in a deoxidising atmosphere. By this means the lead melts and flows into a sump or hollow at the foot of the sloping bed of the furnace, leaving the greater portion of the copper it originally contained, together with iron and other impurities, the melting-points of which exceed that of lead, on the furnace-bed. Nearly all the silver present in the lead charged into the furnace, and with it the gold, passes into the liquated product, owing to the low melting-points of the silver-lead and gold-lead alloys there present. This liquated lead, together with the ore-lead, is then submitted to an oxidising fusion in a reverberatory furnace, the result being that the arsenic, antimony, tin,



and other impurities present, which had failed to be eliminated by the liquation process, are oxidised, and a portion of the lead being simultaneously oxidised and fused, they pass into this oxide scum, and can be removed with it. Owing to the varying degree of oxidisability of the several impurities, the fused litharge obtained at different stages of this process contains relatively larger or smaller quantities of the various impurities. These litharges, after removal from the furnace, are kept separate, and are known by the name of the more important impurity they contain. Each of them is afterwards reduced by itself in a small blast-furnace, the product being in each case a readily marketable hard lead, the impure litharge being first fused with a small percentage of carbon to reduce a portion of the lead, and in this way to collect any silver that may be present in the reduced lead formed. Any copper, too, that may have passed into the liquated lead is also oxidised, but the bismuth remains with the lead. Small quantities of the precious metals always pass into the fused oxide layer on the surface of the lead, but by far the larger proportion of that originally charged into the furnace remains with the purified lead. This lead is then treated by the ordinary Pattinson process, the lead being first melted at a low temperature and then allowed to cool gradually, the lead crystals poor in silver being separated from the richer molten portion. This treatment is repeated in the ordinary manner until the poor lead contains 0.1 per cent. of silver. Instead of continuing to treat this lead by the Pattinson process, the Parkes process of desilverisation by the aid of zinc is employed for the purpose of extracting the remaining silver and gold, the lead from this treatment being dezincified by an oxidising fusion, after which it is ladled into moulds and is ready for the market. The rich Pattinsonised lead is cupelled in cupellation-furnaces of the German type, with non-absorbent marl beds. The cupellation is so conducted that the lead, being charged into a hearth of large size, is oxidised until the residual material contains about 80 per cent. of the precious metals. This requires a higher temperature for its further treatment, and it is therefore removed from the large furnace to a similar but much smaller one, in which the remaining portion of the lead is eliminated, the fused gold and silver being granulated by pouring into water, the granules dried, and the gold and silver parted by the aid of sulphuric acid.

The litharge, if of a yellow colour, is reduced to the metallic state by a reducing-fusion in a small Pilz furnace, but any red litharge that is produced is sold as such. The beds of both the large and the small cupellation-furnaces show green spots at the places where the final products, rich in gold and silver, collected; the bismuth, not being removed by oxidation until nearly all the lead has been oxidised, passes into these portions of the marl-beds, colouring them green. These green patches are carefully removed,



dissolved in hydrochloric acid, and the bismuth oxychloride is precipitated by dilution with water. This is either sold as such after purification, or else is reduced to the metallic state by fusion in crucibles with iron. The other portions of the marl cupellation beds, being rich in lead, are on this account added to the various smelting charges.

*Zinc.*—The argentiferous zinc ores are roasted, the sulphurous anhydride evolved being collected and converted into sulphuric acid. The desulphurised ore is then mixed with carbon, and placed in the retorts, which are heated in a regenerative furnace by gaseous fuel. The zinc distils over, and is collected in fire-clay receivers. The residues left in the retorts contain the precious metals, and are charged into the Pilz furnaces with the lead ores.

The zinc rich in silver and gold obtained by the Parkes process is distilled in an ordinary Morgan furnace, which consists of a hooded crucible contained in a wind-furnace. This completes the lead-smelting process proper, both the gold and silver present in the original materials treated having been collected, and the desilverised lead obtained in a form in which it is ready for the market.

The *cupriferous regulus* resulting from the ore-smelting contains usually but a few per cent. of copper, and consists chiefly of the sulphides of iron and lead. It may be mentioned that it is necessary to have considerable quantities of iron present in the furnace-charge, partly on account of the desulphurising action of the reduced metal, and partly because considerable quantities of zinc are usually present, and the zinc-oxide, passing into the slag, would render it exceedingly pasty and difficult to fuse, were it not for the counteracting influence of large quantities of ferrous oxide.

This regulus, if its composition is such that this treatment is admissible, is roasted in kilns, the sulphurous anhydride produced being utilised in the manufacture of sulphuric acid. When roasted the regulus is added to the slag-smelting charge; the greater portion of the lead-oxide contained in the roasted regulus is then reduced to the metallic state, and a second regulus is produced, which is poorer in lead but richer in copper than was the one resulting from the ore-smelting. This regulus is too rich in copper to admit of its being roasted in kilns, the tendency of the pieces of regulus to clot together during the roasting being too great; it is therefore roasted in "stalls" which are built of brick, and much resemble ordinary cattle-stalls; they are roofless, with low surrounding walls and a slightly sloping bed. On this bed wood is placed, the regulus to be roasted being piled up on it, and then covered over with a compact layer of finely divided roasted pyrites or regulus. The stalls are placed in rows side by side, and back to back, a tunnel being left between every two

such rows. Into this tunnel the gases resulting from the roasting are drawn through perforations in the back walls of the stalls, and are led away to the sulphuric-acid chambers. The combustion is started by lighting a small fire in a grate outside the stall; this kindles the wood, the heat evolved by the combustion of the sulphur in the regulus being afterwards sufficient to continue the process without the addition of any other fuel. This roasted second regulus is then treated as before, until a regulus is produced which contains about 35 per cent. of copper.

Instead of this repeated roasting and treatment with the slag-charge, the regulus, after having been roasted, may be treated in a cupola, together with lead-slugs and other fluxing and reducing additions. The product is a comparatively rich regulus, the lead originally present being reduced to the metallic state, taking with it the silver, the enriched regulus retaining but little of the precious metals. When enriched to the degree mentioned above, the regulus is brought, by a single roasting in an ordinary Welsh reverberatory furnace, to a "white" or "pimple" metal containing about 75 to 80 per cent. of copper. This is not further treated at the Müldeuhütte, the principal works at Freiberg, but is sent to the Halsbrücke works, where it is roasted sweet, and the copper converted into copper sulphate by treating the roasted material with sulphuric acid. Any lead and gold that may have been present remain undissolved, as does also the greater portion of the silver, the small quantity that passes into solution being reprecipitated by metallic copper. The undissolved lead residue is added to the blast-furnace treatment.

*Speise.*—This is a comparatively rare product. The nickel and cobalt it contains are concentrated by a process resembling that for the concentration of the copper in the regulus, the speise being first roasted and then re-melted with fluxes, such as lead-slugs, and with reducing agents, in a small blast-furnace. Metallic lead is obtained, which contains the greater portion of the precious metals originally present in the speise, and the latter is much richer in nickel and cobalt after this treatment than it was before. In this concentrated state it is sold to outside works, where it is treated by the wet process, the residues, which contain the gold and silver of the speise, being bought back by the Government works.

The *ore-slag* is treated in the manner that has been described, the resulting slag, poor in lead, being thrown away. This contains about  $2\frac{1}{2}$  per cent. of lead and 0.0045 per cent. of silver, the zinc-oxide also present occasionally reaching some 20 per cent.

The *fume* contains large quantities of lead-oxide, together with zinc-oxide and arsenious anhydride, which is collected and sold after a further sublimation. The oxides of lead and zinc remain on the bed of the furnace, and are added to the blast-furnace charge.

Thus, the general scheme of treatment is as follows:—The ores are mainly those of lead, copper, zinc, and silver. The products are lead, zinc, bismuth, silver, gold, arsenic, as metals, and copper, mainly recovered as sulphate. Besides these, there are also incidental products, such as sulphate of iron and sulphate of manganese. Nickel and cobalt are recovered as arsenides—that is, in the form of speise; and the arsenic is recovered partly as metal, but mainly as powdery arsenious anhydride, and as red, yellow, and white arsenical glass.

The ores come partly from surrounding mines, and partly from foreign sources, the latter being smelted mainly for the copper, silver, and gold they contain. Almost all the ores are argentiferous. The principal portion of each charge consists of lead ores, and these are divided into galenas with 30 per cent. or more of lead, and poor lead ores with 15 to 20 per cent. In the mean they contain generally 40 per cent. of lead, and 0·015 per cent. of silver. The lead in the ore is only paid for when it reaches 15 per cent., additional payment being made for every 5 per cent. above 20 per cent.—that is, for 25, 30, 35, and so on. Those ores in which only the silver or gold is of a value sufficient to cause them to be paid for are called “Dürrerze,” and the class is subdivided into—pyritic, 20 to 40 per cent. sulphur; quartzose, 10 to 19 per cent. sulphur; and spathose, 0 to 9 per cent. sulphur.

The sulphur is paid for when it exceeds 24 per cent., and every additional 5 per cent. is paid for. Each per cent. of copper is paid for, but fractions of 1 per cent. are not taken into account.

The zinc ores must not contain more than 5 per cent. of lead, and in ores that are not described as zinc ores, only 3 to 4 per cent. of zinc may be present.

The copper ores contain from 1 to 15 per cent. of copper, arsenical ores from 10 per cent. arsenic, zinc ores from 30 to 40 per cent. zinc, sulphur ores from 25 per cent. sulphur.

The arsenic in an ore is paid for when it reaches 10 per cent., and fractions of 5 per cent. are accounted for.

Gold is paid for from 0·0005 per cent. and upwards, and silver 0·004 per cent. and upwards.

The weighing takes place in the presence of representatives of the mine and of the works. About 5 cwt. is weighed at a time. The accuracy of the weighing depends on the richness of the ore; 0·01 to 0·05 per cent. silver accurate to 1 lb., 0·50 to 5 per cent. silver accurate to 0·1 lb., 5 per cent. and upwards, accurate to 0·02 lb. Ores rich in gold are always weighed to 0·02 lb.

*Sampling.*—A small scoopful is taken from every 2 cwt. and is thrown into two or more wooden dishes, according to the amount weighed off. The ore is then put into the ore-house, and a board is inserted in the ore-heap, showing the character of the ore, its quality, etc. The moisture is determined by heating 75 grammes in a copper shovel; the calculation of the moisture is accurate



to  $\frac{1}{2}$  per cent. The mixing takes place in the ore-house. The various ores are spread out in layers, the thickness of which depends on the nature of the material, layer over layer. Then a definite portion is cut off one end of the heap, and the ore so removed is thrown up into a conical heap, which is then considered to be sufficiently mixed.

*Roasting.*—Heaps of from 6000 cwt. to 7000 cwt. supply four roasting-furnaces for a week and a half; one furnace will treat 180 cwt. a day. The roasting-furnace is a single-bedded reverberatory, upwards of 40 feet long and about 10 feet broad; it has eleven doors on each side, and one, which is used for roasting pure galena, has fifteen doors on each side. It is worked from both sides at the same time. The fire-bridge is hollow, and the bed consists of a layer of fire-bricks, made from two parts of raw and one part of burnt clay; they contain 60 to 70 per cent. of silica. These bricks rest on common bricks supported by an iron plate, resting in turn on pillars. If the hearth, or fire-bridge, becomes worn the work is not stopped, but, by means of a long iron ladle, a ball consisting of one part of clay and two parts of poor quartz ore, is inserted. This is beaten down so as to repair any defective place.

Each charge of ore consists of 34 cwt., and there are five such charges on different parts of the furnace-bed at one time. The charge near the fire-bridge is allowed to clot, and is then removed. The other charges on the furnace-bed are then advanced towards the fire-bridge the distance of two doors at a time. The fireplace is divided in the centre, so that really there are two fireplaces, or grates, to each furnace, as the breadth is too great to permit one fireman to stoke the whole.

These long-bedded calcining-furnaces are in connection with long brick chambers for the condensation of the fume, the collection of which takes place every six months, when some 2700 cwt. to 3000 cwt. of material is collected, containing—0.01 to 0.02 per cent. silver, 10 to 28 per cent. lead, 40 to 50 per cent. arsenious anhydride. The sulphurous anhydride from these flues cannot be used, as the gases are far too dilute and impure.

The charge for roasting generally consists of—galena, 30 to 40 per cent.; poor lead ore, 20 to 30 per cent.; poor quartzose ore, 10 to 15 per cent.; and residues, 5 to 10 per cent.

The roasted ore still contains from 5 to 7 per cent. of sulphur when the semi-fluid charge is withdrawn from the furnace into barrows of sheet-iron. The roasted charge is tipped out when solid, and broken into pieces about the size of the fist, and sorted by sight into (1) well roasted, (2) ordinary, and (3) badly roasted, according to whether much or little undecomposed galena is seen to be present. The men are paid accordingly.

There are several large Pilz furnaces, each with eight tuyères, and one small one with four tuyères. The following is a charge



for the ore-smelting:—Ore, 450 cwt. ; pyritic ore, 80 cwt. ; roasted residues, 40 cwt. ; slag, 550 cwt. ; quartzose ore, 20 cwt. ; total, 1140 cwt. This gives 88 cwt. of argentiferous lead, containing 0·4 to 1 per cent. of copper, and 20 cwt. of regulus, and very often a speise forms as well. In charging, the coke is thrown towards the centre, and the larger pieces of ore to the side.

If an obstruction or “bear” forms in the furnace, it is usually a ferruginous one ; but it may contain much zinc-sulphide, and it generally forms at the top of the boshes. In order to remove it, bricks are removed below the bear, and the obstruction is knocked away while hot. The bear often has the form of a ring. The hearth of the furnace is built upon an iron plate. Then follow three layers of common bricks placed flat, and then two layers of fire-bricks, these together being about 16 inches thick. Then follows another layer, 16 inches thick, of the fire-bricks already described. The pressure of the blast is about  $10\frac{3}{4}$  to  $13\frac{1}{4}$  inches of water when smelting ore, and 7 to 10 inches when smelting slag.

The hearth is allowed to fill until some of the regulus is seen to come out with the slag, which is tapped continuously from one or other of two tap-holes.

The lead contains . . .	0·5 to 0·6	per cent. of silver.
The lead regulus . . .	25·0 ,, 30·0	,, ,, lead.
	6·0 ,, 15·0	,, ,, copper.
	0·2 ,, 0·25	,, ,, silver.

The slags contain 0·3 per cent. of copper, 4 to 5 per cent. of lead, 0·003 to 0·004 per cent. of silver.

*Smelting the Rich Slag.*—The slags may be viewed as three equivalents of monosilicate with one equivalent of bisilicate, and slags that do not contain more than 0·001 to 0·002 per cent. of silver and 1·5 per cent. of lead are thrown away.

The charges in slag-smelting are very varied. The following are examples:—

(1) Slag, 900 cwt. ; plumbiferous material, 45 cwt. ; broken-up hearths, 12 cwt. ; which yielded 52 cwt. of poor lead, 85 cwt. of coke being required.

(2) For every 2 cwt. of a mixture of 5 cwt. roasted regulus from slag, 12 cwt. roasted ore-regulus, 2 cwt. roasted copper-regulus, and 5 cwt. roasted liquation-residues, is added  $4\frac{1}{2}$  cwt. of slag from galena-smelting, and 4 cwt. of common slag.

(3) Three cwt. of ore-slag, 3 cwt. of various residues rich in lead,  $1\frac{1}{2}$  cwt. once-roasted ore-regulus, 0·5 cwt. of coke. To this charge there is added, in the working-day of twenty-four hours, 12 cwt. of marl, 12 cwt. of hearth, and 12 cwt. of lead-skimmings.

(4) Twelve cwt. of slag, 25 cwt. of twice-roasted regulus, 40 cwt. of slags from the smelting of the litharge.

*Products of the Slag-smelting.*—Slag-lead containing 0·4 per

cent. of silver, regulus containing 10 to 20 per cent. of lead, or regulus containing 20 to 30 per cent. of copper, poor slag containing 0.0015 per cent. of silver and 1.5 to 2 per cent. of lead.

Sometimes a speise of nickel and cobalt is also formed. The regulus is only about one-third of the amount of lead produced. The slags often contain 9 per cent. of oxide of zinc. The regulus is broken up and roasted in kilns, or stalls, and is then added to a smelting charge similar to that by which it was formed, or is concentrated in a Pilz furnace, or goes to a reverberatory for concentration with silica and barium-sulphate.

*Smelting the Speise.*—The charge is 150 cwt. of speise, 675 cwt. ore-slag, 4 cwt. impure litharge, 44 cwt. lead residues, 5 cwt. hearth, 40 cwt. fluorspar, 75 cwt. coke. The products are 54 cwt. of lead, 12 cwt. concentrated speise.

The speise is concentrated by continuous and alternate roastings and smeltings, until it contains 20 per cent. of nickel, when it is sold. The poor lead goes to the liquation-furnace. The regulus is roasted in kilns and stalls, then fused to concentrate it, until it contains 30 per cent. of copper; it is then called "copper" regulus. It is afterwards treated in a reverberatory to form pimple metal. Incidentally, large quantities of impure lead and substances containing lead-oxide are produced.

The process employed for the reduction of the lead from such substances consists of a reducing-fusion. One such substance, the litharge derived from the rich argentiferous lead, contains about 78 per cent. of lead. The furnace used is a small Pilz furnace with four tuyères. The charge in twenty-four hours is 1500 cwt. litharge, 450 cwt. lead-slugs, 50 cwt. slags from a previous smelting, 130 cwt. coke. The products are (1) a variety of lead, which, according to its purity, is either first liquated and then refined, or is taken to the Pattinson pots, and (2) a slag containing 10 per cent. of lead. Part of this slag goes to the next charge, and part to the first ore- and slag-smelting.

*Liquating the Impure Lead.*—This is done at Freiberg on the inclined bed of a reverberatory furnace, 500 cwt. being treated daily. The copper, with some lead, remains solid in the form of liquation-residues. The lead, before the liquation, contains 0.5 per cent. copper, afterwards it still retains 0.07 per cent. The residues are about 5 per cent. of the total lead; they consist principally of lead with 15 to 18 per cent. of copper, and are added to the slag-smelting in the Pilz furnace.

The scum from the Pattinson pots is also treated in this reverberatory, in admixture with lignite. When antimonial lead is liquated the temperature must be kept low, but a little wood must be kept kindled in the well of the furnace to prevent the lead solidifying.

If the lead contains 1.5 per cent. of silver, it is cupelled at once—that is, it is added to lead that has been already enriched

by the Pattinson process. If it is impure, the lead is refined and Pattinsonised.

In refining, the lead is fused in an oxidising atmosphere on the bed of a reverberatory furnace. The products are a variety of different kinds of litharge to which the name of *Abstrich* is given. They are nothing but impure litharge, and, as the nature and proportion of the impurities vary greatly, the appearance is very dissimilar; some are dark-grey and stony, others are light-yellow and are crystalline in structure:—(1) Powdery tin *Abstrich*; (2) fused tin *Abstrich*; (3) arsenical *Abstrich*; (4) antimonial *Abstrich*; (5) impure litharge *Abstrich*; (6) pure litharge *Abstrich*. There is a fractional oxidation of the various impurities, the tin and arsenic going first. The time required to refine 400 cwt. of lead is about fifty hours.

The products, in the case of lead smelted from ore, are as follows:—10 cwt. of tin *Abstrich*, or about 3 per cent. of the total lead, containing 11·3 per cent. of tin, 14·4 per cent. of arsenic, 2·8 per cent. of antimony; 20 cwt. arsenical *Abstrich*, or about 5 per cent. of the total lead, containing 8·5 per cent. of antimony, 8·9 per cent. of tin, 8·7 per cent. of arsenic; 10 cwt. of antimonial *Abstrich*, about 3 per cent. of the total lead, containing 6·8 per cent. of antimony, 1·3 per cent. of tin, 4·4 per cent. of arsenic; 10 cwt. impure litharge, about 3·2 per cent. of the total lead, containing 3·1 per cent. of antimony, 0·5 per cent. of tin, 2·0 per cent. of arsenic.

In refining lead produced from the smelting of slag, very similar varieties of *Abstrich* are obtained, except that they are not so rich in tin, as when lead from ore is refined. At the Halsbrücke works, a hollow pipe through which steam is passed is sometimes used as a mechanical stirrer when refining. In desilverising the tin *Abstrich*, about 90 cwt. of slag-lead is placed on the bed of the refining-furnace and then, on that, 15 cwt. of the *Abstrich*, mixed with 4 per cent. of coal; the charge is melted down in three hours, and then another 15 cwt. of *Abstrich* and 4 per cent. of coal is added, and so on until the furnace is full. The desilverised *Abstrich* is taken off (the silver passing into the lead) and run down in a small Pilz furnace.

The lead is refined and Pattinsonised. The antimonial *Abstrich* is desilverised in the same manner, except that 24 cwt. of it is added instead of 15 cwt., as it melts easier. The arsenical *Abstrich* and impure litharge are directly revived by being run down in a small Pilz furnace for metallic lead, the lead obtained being then refined. The impure lead is added in part as a plum-biferous addition to the Pilz furnace smelting ore.

The desilverised tin *Abstrich* is smelted in a Pilz furnace, the charge being 100 parts of *Abstrich* to 100 to 150 parts of poor lead-slag, 50 per cent. of slags from the same working, and 20 per cent. of limestone. The lead obtained is revived and poled in



a Pattinson pot. The various kinds of *Abstrich* obtained are desilverised over and over again, until they contain comparatively no silver. The composition of the hard lead obtained from the stanniferous *Abstrich* is very varied. One variety contains 18 per cent. of tin, 10 per cent. of antimony, and 2 per cent. of arsenic.

The desilverised antimonial *Abstrich* is smelted in a Pilz furnace with slag and 10 per cent. of limestone. In twenty-four hours 100 cwt. to 150 cwt. are sent through. The hard lead is liquated and poled, and contains about 10 per cent. of antimony, 3 per cent. of arsenic, and 1 per cent. of tin. Each refining-furnace is worked by one refiner and two assistants.

*Pattinson Process as conducted at Freiberg.*—In this process, the silver is concentrated in fluid lead by straining off crystals of lead which separate from the bath. The pots have a thickness at the bottom of 2·36 to 2·76 inches, and 1·9 inch at the sides. They are 5 feet in diameter at the top, and 2 feet 9 inches at the bottom. They hold about 15 tons, and last about 500 crystallisations. Each pot has a separate fire; there are sixteen pots, sometimes worked in two batteries of eight pots each. They are worked by the one-third system. Each pot is kept at a determined percentage of silver, and assays are made daily. When fresh lead is added, it is introduced into the pot containing the same percentage of silver. At Freiberg it is usually the third pot from the left. The rich lead contains from 1·5 per cent. to 2 per cent. of silver, and the poor 0·0018 per cent. The scum from pots 1 to 4 is liquated by itself, and similarly those from pots 5 to 8, and from 9 to 15 by themselves. In a case in which the enrichment had not been carried far enough, the following were assays of the contents of the pots:—(1) 1·07 silver, (2) 0·80 silver, (3) 0·42 silver, (4) 0·33 silver, (5) 0·30 silver, (6) 0·26 silver, (7) 0·18 silver, (8) 0·11 silver, (9) 0·08 silver, (10) 0·04 silver, (11) 0·02 silver, (12) 0·012 silver, (13) 0·007 silver, (14) 0·0035 silver, (15) 0·0015 silver, (16) 0·001 silver. The poor lead never contains more than 0·05 per cent. of copper, 0·2 per cent. of iron, and traces of arsenic and antimony. The fuel used is a mixture of lignite and small coke. To each battery of sixteen pots there is one fireman, and to every two pots there are two men. There is also one lead ladler. The men work for eleven hours, but the fireman works for twelve hours.<sup>1</sup>

*Cupellation at Freiberg.*—The hearth is formed of 48 cwt. of fresh marl mixed with  $\frac{1}{2}$  cwt. of clay. The marl is of three kinds:—

	I.	II.	III.
Calcium carbonate . . . .	50	68	66
Magnesium carbonate . . .	13	27	6
Iron carbonate . . . . .	2	2	2
Clay . . . . .	14	3	25

<sup>1</sup> Pattinson's process is now supplemented by Parkes' process, a joint-process being used.



Any pyrites present is carefully removed.

The greatest depth of the hearth from a line on a level with the tuyères ought not to be more than 7·8 inches. The fire-resisting material with which the roof is lined consists of one part of clay and two parts of silica; 100 cwt. to 200 cwt. of lead is placed on the damp hearth, and this is covered with sawdust and chips; the roof is then put on, the wood lit, and the roof luted on with clay; the fire is kindled, and the blast turned on; the lead melts down in sixteen to eighteen hours. The temperature is gradually raised, and lead is added, 700 cwt. being the total charge. The litharge, as it forms, is removed until the remaining lead on the bed contains 60 to 80 per cent. of silver. This is taken out, and the extraction of the silver completed on a similar but much smaller hearth. If the red litharge obtained contains less than 0·02 per cent. of silver, it is sold. It is said that if the lead contains 0·2 per cent. of bismuth no red litharge will be produced. At the end of the process, where the concentrated lead and silver settle on the hearth, there is a dark spot which indicates the presence of bismuth, and which is broken away and the bismuth subsequently extracted, this portion of the hearth having been previously hollowed to collect the rich lead. There are two men attending to each furnace, and it requires 120 to 140 hours to cupel 700 cwt. of lead. The silver obtained is granulated by running it into water. It is about 990 fine, and is sent to the Halsbrücke works to have the gold parted from it.

*Solution of the Regulus.*—The concentrated copper regulus is sent to the Halsbrücke works, where it is roasted nearly sweet. It still contains about 1 per cent. of sulphur. It is then passed through a rather fine sieve, and the larger pieces are crushed and re-roasted. The roasted regulus is dissolved in sulphuric acid in wooden vats lined with hard lead. The sulphate of copper is crystallised out, and, after purification by re-crystallisation, is sold. Such copper sulphate as does not crystallise out but remains in solution is removed by scrap-iron. The solution of copper sulphate before crystallisation is made to pass over metallic copper, in order to remove any silver it may contain. The residue, after the treatment of the regulus with sulphuric acid, contains the lead, and most of the silver originally present in the regulus treated. This is sent back to the Pilz furnace, with a view to concentrate the silver in the lead produced from the lead ores.

**Wet Processes for Treating Argentiferous Copper Ores.**—In certain cases copper pyrites is converted into copper sulphate by the action of air and moisture. The sulphate is dissolved in water, and the copper precipitated from the solution by iron. When, however, argentiferous ores are dealt with, containing much copper but not much lead, the processes are more complicated. These processes are illustrated by the following examples:—

1. Ziervogel's process, which consists in submitting the regulus to an oxidising roasting, yielding cupric oxide and silver sulphate.

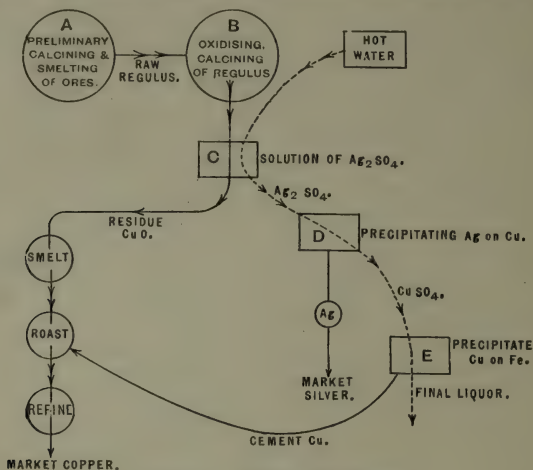


FIG. 184.—Ziervogel Process.

The latter is dissolved in water and precipitated on copper. The cupric oxide is recovered from the residues by smelting (fig. 184).

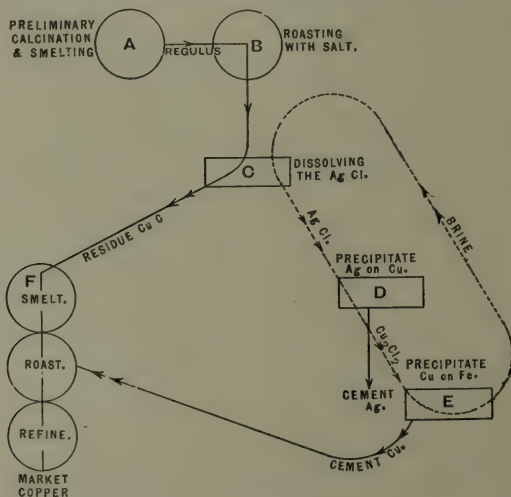


FIG. 185.—Augustin Process.

2. Augustin's process, which has now been superseded by other methods, consisted in submitting the regulus to an oxidising and subsequently to a chloridising roasting, yielding cupric oxide and

silver chloride. The latter was dissolved in hot brine and precipitated on copper. The cupric oxide was recovered from the residues by smelting (fig. 185).

3. Longmaid's or Henderson's process, which is applied to the ore after roasting, and which consists in dissolving the copper and silver from the ore roasted with salt by water and dilute hydrochloric acid. The copper is precipitated by scrap-iron, and the silver is recovered by the Claudet process (fig. 186).

4. In Claudet's process the silver is precipitated as silver iodide from a solution of copper and silver chlorides by zinc iodide regenerated during the process, zinc being used to precipitate the silver.

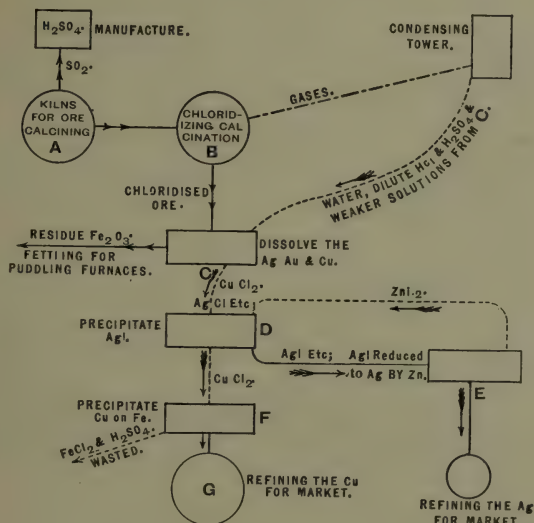


FIG. 186.

These processes are illustrated by the accompanying diagram, Claudet's process forming part of the scheme (fig. 186).

The plant used in the Ziervogel process is illustrated in fig. 187.

The charge of roasted material is placed in tubs A, provided with false bottoms, and hot water is introduced through the pipe *b* until the liquors begin to flow through the tap *c*. The pipe *b* is then closed, and acidulated hot water is admitted through the pipe *a*. The silver sulphate solution flows into a long tank, divided into two compartments B, C, whence it is distributed into precipitating tubs D, provided with false bottoms on which cement copper is placed, with copper bars above it. Most of the silver is precipitated, and the liquors pass to a trough E, on the bottom of which is a layer of pieces of sheet-copper, and thence

to the tubs F, also containing a little copper. The desilverised liquors are conveyed by the gutter *g* to a leaden pan, and again utilised. The precipitated silver is treated with sulphuric acid in the tubs H, and finally washed with hot water. The liquors rise through L, and are conducted by the trough M over metallic copper into tanks containing scrap-iron. The water from the final washing is run off at N, and conducted to a lead-lined tank. The silver is moulded into blocks and refined.

**Treatment of Gold Ores.**—Plattner's method of extracting gold from its ores by means of chlorination is based on the fact that chlorine gas transforms gold into soluble gold chloride without sensibly attacking the earths or metallic oxides with which the gold is mixed.

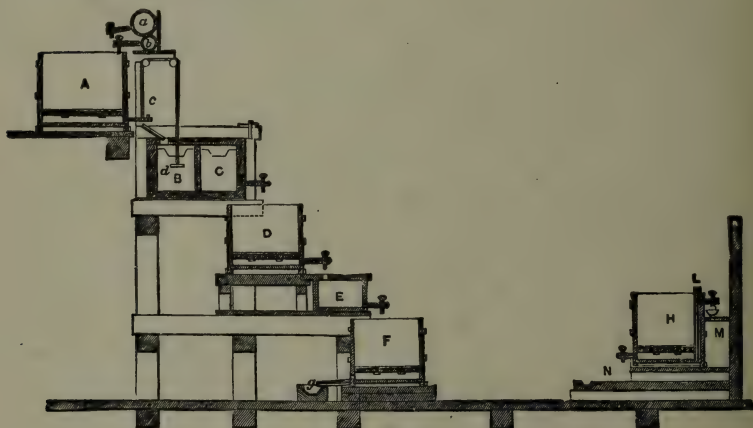


FIG. 187.

The ore is crushed and roasted with salt, 5 to 9 lbs. of salt per ton of ore having been added. Any lead, bismuth, or silver present is thus converted into chloride. The iron sulphide present, however, will first be converted into iron sulphate, and this must be decomposed to form ferric oxide by raising the temperature of the roasting-furnace. The base chlorides are soluble in water, and are removed by treating them in wooden vats. The residue is then acted upon in a moist state in wooden, pitch-lined vats by gaseous chlorine. The gold is thus converted into chloride, but the ferric oxide remains unchanged. The gold chloride is dissolved in hot water, and precipitated by ferrous sulphate solution in another set of wooden vats. The insoluble residues left in the "gassing" vat are now treated with sodium hyposulphite solution in order to remove the silver chloride, which may be precipitated by means of calcium sulphide and reduced by heating in air.



Numerous modifications of the chlorination process<sup>1</sup> have been introduced, and large sums of money have been sunk in the formation of companies to work the processes. In many cases very satisfactory results have been obtained, more especially where the process has been applied to the treatment (after roasting) of the sulphurets constituting the "concentrates" from the Frue Vanners, over which the tailings from the stamp batteries are allowed to pass.

Dr Mears, of Philadelphia, was the first to lay stress on the influence of pressure in increasing the solvent action of chlorine. With certain ores, however, it has been found that as good results are obtained without pressure as with the highest pressure.

The largest chlorination plant in the world in 1890 was at the Mount Morgan mine in Queensland. According to M'Dermott and Duffield,<sup>2</sup> the ore averages 5 oz. of gold per ton, and 1500 tons is worked per week, while the tailings contain only 3 dwt. per ton. The process consists in drying, crushing between rolls, roasting, and working in revolving barrels by the aid of chloride of lime and sulphuric acid. The ore is roasted for two and a half hours, and worked in wooden barrels 5½ feet in length. Each barrel takes a charge of 1 ton of ore, with 30 lbs. of chloride of lime, 33 lbs. of sulphuric acid, and 80 gallons of water. The gas-pressure does not exceed 20 lbs. per square inch at its maximum development. The barrels are slowly revolved for two hours, and the charge is then filtered on gravel and sand beds, and the solution precipitated by filtration through charcoal filters, which are subsequently burnt in a reverberatory furnace. A method of leaching with chlorine water has more recently been introduced at Mount Morgan.

Of late years the MacArthur-Forrest process and its modifications have come into much prominence for the recovery of gold from the "tailings" from amalgamation plant working upon ores of all grades, for the direct treatment, in some cases, of low-grade ore, and also for the treatment of silver ores. It consists in the treatment of the mass of finely divided material with a very dilute solution of potassic cyanide for a period of about twenty-four hours. Cyanide of gold is formed, soluble in the excess of reagent, and the solution is run over metallic zinc upon which the gold is precipitated. By this means very large quantities of gold are now annually recovered that would, owing to the cost of treatment by the older methods, have otherwise been lost.

The development of this process, which has almost completely replaced the chlorination process, has assumed gigantic proportions in South Africa, Australia, New Zealand, and America, where plants have been erected capable of dealing with enormous quantities of material. A full description of the plant and

<sup>1</sup> Rose, *Metallurgy of Gold*.

<sup>2</sup> *Losses in Gold Amalgamation*, London, 1890, p. 30.

methods of working is given by Rose,<sup>1</sup> but a few general remarks may be made. As already stated, the "Cyanide Process" has been applied chiefly to the treatment of "tailings" from stamp batteries. This material, which has generally passed a 25- to 30-mesh screen, is first sorted by Spitzluten and Frue Vanners, the fine sands and slimes being conveyed to separate vats for special treatment. The concentrates from the Vanners, consisting chiefly of pyritic material, are also treated separately.

The main bulk of the tailings is conveyed to vats often 40 feet in diameter and 7 feet deep. These vats are of wood, concrete, or steel, and are provided with false bottoms on which rest filter-beds of cloth and pebbles, suitably supported to bear the weight of the "tailings." Before the leaching operation proper, which is effected with dilute solutions of potassium cyanide usually containing from 0.05 to 0.35 per cent., care is taken to neutralise any acidity in the "tailings" by means of soda or lime, and so prevent undue losses of cyanide. After leaching, which usually occupies from twelve to twenty-four hours, the cyanide solutions containing the gold, dissolved as the double cyanide,  $\text{KCy}, \text{AuCy}$ , are drained off from the vats and conveyed to the precipitation plant. The particular form of this plant varies considerably. The original method consisted in allowing the solution to flow through a series of boxes containing zinc shavings on which the gold was deposited. This method, with certain modifications to admit of its use with very dilute solutions, is still largely employed. The chief rival to this method is the electrical precipitation on lead cathodes by Siemens and Halske, who claim for it many advantages over the original method of precipitation by zinc. Precipitation by zinc dust and charcoal have also been employed.

In modern practice the whole of the material from the stamp batteries is slimed by passing through tube mills, then agitated with the cyanide solution, and passed through filter-presses. Vacuum filter-presses of various makes are being largely used at the present time. In order that ores may be successfully treated by the cyanide process, certain essential conditions must be fulfilled, such as:—

1. Sufficiently fine grinding to allow the solution to come into intimate contact with the gold.

2. The gold itself should be in a fine state of division, for coarse gold dissolves in the cyanide solution extremely slowly.

3. The absence of interfering bodies, some of which may occur owing to the oxidation of pyrites, etc., present in the ore. A preliminary wash with water takes away interfering soluble salts, whilst a preliminary wash with alkali neutralises the effect of acid present.

4. The absence of gold in combination with various elements. When the gold is present in combination with tellurium, bismuth,

<sup>1</sup> Rose, *Metallurgy of Gold*.

etc., simple cyanide treatment is not efficient, and sometimes a preliminary roast is found to improve matters.

5. The character of the gangue is also of importance, as difficulties are met with in treating certain ores, containing kaolin, talc, clay, etc. For kaolin and talc sliming is good, and for clay a preliminary roast is often used.

**Purification of Platinum.**—The methods of treating the metals of the platinum group present features of much interest; the use of both “dry” and “wet” operations being involved. The crude native metals are first treated in a reverberatory furnace, with an equal weight of galena. Some of the lead will be reduced to the metallic state by the iron present in the charge, and will form an alloy with the platinum, rhodium, palladium, and some of the iridium present. Any osmiridium present will not alloy, but will settle down to the bottom of the fluid mass; whilst the earthy impurities are fluxed off by the addition of glass and borax. Litharge is then added to oxidise the remaining sulphur, the slag is skimmed off, and the metal is run into ingots. The metal is then cupelled, and yields platinum and the other members of its group. To purify the mass, it is melted with six times its weight of pure lead, is granulated, and treated with dilute nitric acid. The insoluble black powder, forming a residue, contains all the platinum and iridium present in the lead, together with small quantities of the other metals, and it is treated with dilute *aqua regia*, which dissolves out the platinum and the residue of the lead, but does not attack the iridium. The solution of chlorides is filtered off, evaporated to a small bulk, and the lead precipitated by sulphuric acid. A mixture of sodium and potassium chlorides is added to the filtrate, which is then heated to 80° C., and left to stand for several days. Most of the rhodium present remains in solution, and the precipitate of platinum-potassium chloride is collected and washed with a solution of ammonium chloride, and then with water. As some rhodium may still be present, the chloride is dried, and mixed with potassium bisulphate and a little ammonium sulphate; the whole is then heated in a platinum vessel until the platinum is completely reduced. The mass is thoroughly washed with water, and the rhodium removed as soluble bisulphate, the pure platinum sponge is finally melted under the oxyhydrogen blowpipe upon a lime crucible.

**Wet Process for Treating Nickel and Cobalt Ores.**—The wet methods for the extraction of nickel and cobalt from a complex regulus or arsenide consist, in the first place, of a roasting operation having for its object the volatilisation of the sulphur and arsenic, and, it may be, antimony, and the conversion of the iron, nickel, cobalt, and other metals present into oxides. Ferric oxide formed in this manner at a high temperature is but little soluble in acids, whilst the other oxides may be readily dissolved. On treating the roasted material repeatedly with hydrochloric acid or with



dilute sulphuric acid, a residue is obtained containing but little or no cobalt or nickel, and consisting mainly of ferric oxide. Some iron will, however, have passed into solution. Should the solution contain lead, bismuth, or copper, these metals may be precipitated by sulphuretted hydrogen; but it is customary to precipitate the copper at a later stage of the operations. The bismuth, too, may be precipitated from a hydrochloric acid solution by dilution with water.

The next operation consists in the precipitation of the iron. Any ferrous oxide which may have passed into solution is converted into ferric oxide by careful addition of chloride of lime, followed by the addition of lime, which precipitates the iron. Arsenate of iron is, at the same time, also precipitated if arsenic is present. Should the temperature of the solution exceed  $40^{\circ}\text{C}$ . some nickel and cobalt are precipitated, as also is some copper.

Instead of an addition of lime as a precipitant, caustic soda or sodium carbonate is occasionally employed to prevent the precipitation of calcium sulphate when working with sulphuric acid solutions. Care must be taken to avoid using an excess of the precipitant, as the precipitation is a fractional one, and, as soon as the iron has been precipitated, oxides of the other metals present begin to be thrown down.

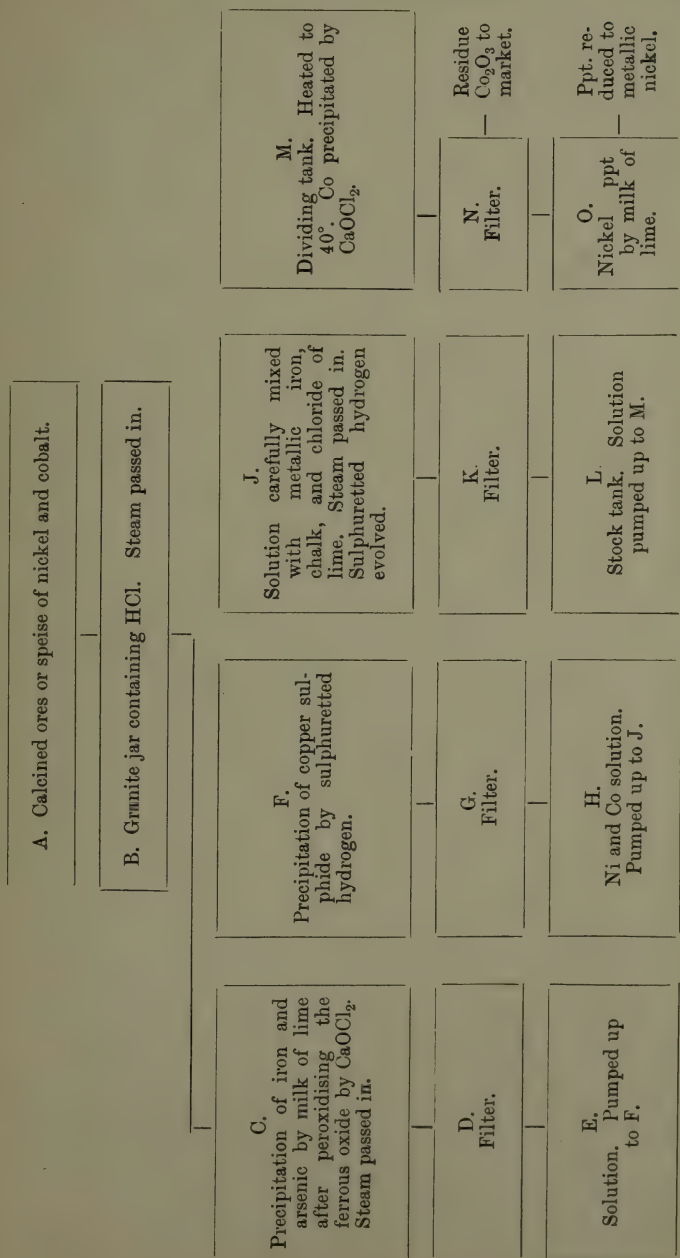
The next stage of the process consists in the precipitation of the copper. This is effected by raising the temperature of the solution to  $70^{\circ}\text{C}$ ., and then precipitating the copper by the careful addition of either calcium carbonate, milk of lime, or a solution of soda. If an excess of the precipitant is employed, nickel will be thrown down. When a test with potassium ferrocyanide shows that the whole of the copper has been thrown down, the cobalt is precipitated from the filtered solution by the careful addition of a solution of chloride of lime to the perfectly neutral, hot, and not too dilute filtrate. If too much chloride of lime is added the precipitate becomes nickeliferous, and this must be carefully avoided. The nickel is next precipitated, either by calcium carbonate, milk of lime, or soda. The nickel hydrate is filtered, dried, heated with sodium carbonate, to decompose any calcium sulphate that may be present, washed with acidulated water, and finally dried and reduced by carbonaceous materials to the metallic state.

This process, being dependent on the fractional precipitation with the same precipitants of the several metals present in the ore or metallurgical product under treatment, is frequently subject to slight alterations of procedure, and the following is a description of the process as carried out at a works in the United Kingdom:—

About 3 cwt. of fine ore or speise A, that has been thoroughly roasted, is charged with hydrochloric acid in granite jars, into which steam is passed. The mass is kept boiling for twelve hours.



## WET PROCESS FOR EXTRACTING NICKEL AND COBALT.



It is allowed to settle, and run off into tubs C. Steam is conducted into the tubs, and when the liquid begins to boil, bleaching powder (chloride of lime) is added to peroxidise the iron, and the mass is allowed to boil for about three hours. The arsenic and iron come down together. If no iron be present in the solution some must be added. The liquid is then run off through filters D, to underground tanks E, whence it is pumped to tanks F, in which the mass is treated with sulphuretted hydrogen. Adjoining these tanks, of which there are six, there are also three lead retorts, in which sulphuretted hydrogen is produced. In these tanks the copper is precipitated, and the nickel and cobalt solution is strained through filters G, and drains into a second underground tank H. It is then pumped into a tank J, and there successively mixed with iron, chalk, chloride of lime, and water from tubs placed above the tank, with a view to precipitate, first, any copper that may have passed into solution during filtration, and then the iron which has taken the place of the copper. The charge is first boiled by the aid of steam pipes so as to expel the sulphuretted hydrogen. It is then run off to a tank L for stock. It is next pumped up into a dividing tank M, and heated with chloride of lime, the cobalt being precipitated as oxide at a temperature of  $40^{\circ}$ . The solution containing nickel is allowed to run off into another tank O, in which milk of lime is added, and the nickel precipitated as hydrated oxide. The liquid is allowed to run off as waste. The oxides are pumped into presses, and the water is drained off. The nickel oxide is dried on the roof of a muffle, heated, and crushed. It is then mixed with charcoal, and heated in a crucible in a reducing-furnace for eight or twelve hours. A rough powder is obtained, and in this form the metal is sold, or the nickel oxide is mixed into a paste with flour and water, which is heated and cut into cubes. These cubes are placed in crucibles with charcoal, and heated to a temperature above the melting-point of copper. The nickel oxide is reduced by the charcoal and by the carbonised flour. The metal does not melt, but preserves the form of cubes. The cobalt oxide is removed from the dividing tanks to stone jars, and treated by a process similar to that described, so as to remove the last trace of nickel. The cobalt is finally sent to market in the form of oxide.

**The Extraction of Nickel from its Ores by the Mond Process.<sup>1</sup>**

—This interesting process marks an entirely new departure, in metallurgical practice, from the principles which have hitherto guided it. It depends on the remarkable property possessed by nickel of forming a volatile compound with carbon-monoxide. When this gaseous compound is heated to  $180^{\circ}$  C. nickel is released in the metallic form. The author was much impressed

<sup>1</sup> This description, taken from a paper communicated by the author to the Institution of Civil Engineers, in 1898, has been slightly modified, and kindly revised by Dr Langer.

during a visit to Canada with the Imperial importance of the great nickeliferous district of Sudbury, Ontario, and the description of any new process which affords a hope of hastening the development of this remarkable district should prove to be interesting. The deposit itself presents many points of interest. According to Professor Coleman of Toronto, the nickel ores of Ontario resemble the gold ores of Rossland in British Columbia, as they consist of a mixture of pyrrhotite (magnetic pyrites) and copper pyrites. These sulphides form enormous masses near the margin of large areas of diorite, or weathered gabbro of Huronian age, the amount of nickel contained in the ore averaging between  $2\frac{1}{2}$  per cent. and 10 per cent., the lower proportion being the more common. It is worthy of note that pyrrhotite from other parts of the country, found in association with Laurentian rocks, is almost barren of nickel. The importance of the nickel deposits of Ontario may be judged from the fact that, until the mines in the Sudbury region were worked, the world's supply of the metal was drawn chiefly from the mines of New Caledonia, an island in the Southern Pacific, supplemented by the Gap mine in Pennsylvania, and a few isolated mines in Norway and Hungary. The extent of the Sudbury deposits is greater than any of these, and New Caledonia, which belongs to France, is virtually the only rival of Ontario in the production of nickel.

The ore at Sudbury is smelted into a regulus, or matte, which contains between 12 per cent. and 20 per cent. of nickel, and about the same amount of copper. This matte may be enriched by suitable treatment, and is "Bessemerised" into a regulus which contains about 40 per cent. of nickel, and is specially free from iron, as the following analyses show:—

ANALYSES OF BESSEMER MATTE UNROASTED.

	I.	II.
	Per cent.	Per cent.
Nickel . . . .	40·938	31·35
Copper . . . .	45·714	48·86
Iron and ( $\text{Al}_2\text{O}_3$ ) . . . .	0·405	0·81
Cobalt . . . .	0·136	...
Sulphur . . . .	11·960	...

It is unnecessary to give a history of the metallurgy of nickel, but it may be well to state that Chronstet isolated the metal in the year 1751, and that Bergman confirmed his discovery in 1774. The methods hitherto employed for extracting the metal from its ores are very complicated; they have involved concentrating the nickel either as a sulphide (matte or regulus), or as arsenide (speise) followed by either "dry" or "wet" treatment. In the

case of certain ores, wet methods only have been employed. The metallic nickel has always to be subjected to a process of refining, mainly, as in the case of cast iron, with a view to separate it from associated carbon.

As regards the experiments from which this process was developed, a few brief historical details may be offered. In 1889 Dr Ludwig Mond, F.R.S., in collaboration with Dr Carl Langer, was engaged in working out a method for eliminating the carbon-monoxide from gases containing hydrogen<sup>1</sup> which they wanted for use in their gas battery.<sup>2</sup> In attempting to effect this, they were guided by the observation they had previously made that finely divided nickel has the remarkable property of removing carbon from carbon-monoxide at a temperature of 350° C., converting it into carbon-dioxide, while the dissociation of carbon-monoxide by heat alone, according to Victor Meyer and Carl Langer, remains incomplete at the high temperature of 1690° C. In the course of these experiments, which they carried out in conjunction with Dr Friedrich Quincke,<sup>3</sup> finely divided nickel, formed by reducing nickel oxide at 350° C. by hydrogen, was treated with pure carbon-monoxide in a glass tube at varying temperatures. In order to keep the poisonous carbon-monoxide out of the atmosphere of the laboratory, the gas escaping from the apparatus was ignited. They found to their surprise that while the tube containing the nickel was cooling, the flame of the escaping gas became luminous and increased in luminosity as the temperature sank below 100° C. Metallic spots were, moreover, deposited on a cold plate of porcelain held in this luminous flame, just as spots of arsenic are obtained in applying the Marsh test for that metal. It was also observed that on heating the tube through which the gas was escaping, a metallic mirror was obtained, while the luminosity of the flame disappeared. On examination these metallic deposits were found to be pure nickel. The next step was to endeavour to isolate this curious and interesting nickeliferous compound, by preparing nickel with great care at the lowest possible temperature, and treating it with carbon-monoxide at about 50° C. The amount of the volatile nickel compound in the gases passing through the apparatus was thus gradually increased. The gases issuing from the apparatus were treated with a solution of cuprous chloride to absorb the excess of carbon-monoxide, and in this way a residue of several cubic centimetres of a colourless gas was obtained, containing the volatile nickel compound. By passing this gas through a heated tube the nickel

<sup>1</sup> Ludwig Mond and C. Langer, "Improvements in obtaining Hydrogen," *British Patent* No. 12,608, 1888.

<sup>2</sup> Ludwig Mond and C. Langer, "A New Form of Gas Battery," *Proc. Roy. Soc.*, vol. xlv. p. 296.

<sup>3</sup> Ludwig Mond, C. Langer, and F. Quincke, *Journ. Chem. Soc.*, vol. lvii. p. 749.



and carbon-monoxide were again separated, and the volume of the carbon-monoxide thus set free was found to correspond to about four equivalents of carbon-monoxide to one equivalent of nickel. By further improving the method of preparing the finely divided nickel, and by passing the resulting gases through a refrigerator cooled by snow and salt, the investigators at last succeeded in obtaining the new compound in a liquid state, and were able to produce it with facility in any desired quantity.

Nickel carbonyl in its pure state is a colourless liquid, boiling at  $43^{\circ}\text{C}$ .; it has a specific gravity of 1.3185 at  $17^{\circ}\text{C}$ ., and solidifies at  $-25^{\circ}\text{C}$ . into needle-shaped crystals. It is soluble in alcohol, petroleum, and chloroform; and it is not acted upon by dilute acids or alkalis. It can be readily distilled without decomposition; but, on heating the vapour to  $150^{\circ}\text{C}$ ., it is completely dissociated into its components, pure carbon-monoxide being obtained, while the nickel is deposited in a dense metallic film upon the sides of the vessel in which the compound is heated.

After the production of nickel carbonyl had become easy, Drs Mond, Langer, and Quincke directed their attention to the action of carbon-monoxide on other metals. A series of experiments was made with a view to obtain a similar compound with cobalt, which in its chemical and physical behaviour so much resembles nickel. The experiments gave, however, the unexpected result that, unlike nickel, cobalt will not combine with carbon-monoxide. Experiments were then made with iron, and indications were soon obtained of the existence of a volatile compound of iron and carbon-monoxide; a long time elapsed before this new compound was obtained in a pure state. It was finally isolated in a way similar to that by which the nickel carbonyl had been prepared, and proved to be a somewhat viscous liquid of pale yellow colour.<sup>1</sup> Its specific gravity at  $18^{\circ}\text{C}$ . is 1.4664; and it distils completely without decomposition at  $102.8^{\circ}\text{C}$ . under a pressure of 749 millimetres of mercury. When cooled to  $-21^{\circ}\text{C}$ . it solidifies into a mass of yellowish needle-shaped crystals. Its chemical composition is somewhat different from the nickel carbonyl, as it contains five equivalents of carbon-monoxide to one of iron. The liquid compound, to which the name of iron penta-carbonyl was given, undergoes no change when protected from the action of light; but exposure to daylight for several hours in a sealed tube is attended with the formation of gold-coloured, tabular crystals, and carbon-monoxide is evolved, so that the pressure in the tube rises considerably. The crystals have, when dried, a metallic lustre, and resemble flakes of gold; they contain two equivalents of iron to seven equivalents of carbon-monoxide. None of the other metals which were submitted to

<sup>1</sup> Ludwig Mond and Carl Langer on "Iron Carbonyls," *Journ. Chem. Soc.*, vol. lix, p. 1090.

investigation showed indications of combining directly with carbon-monoxide.

The discovery that in a mixture of metals only nickel and iron would form volatile compounds with carbon-monoxide, and that they could, therefore, be separated from the other metals, was sufficiently important to induce Dr Mond to arrange laboratory experiments with ores containing nickel, cobalt, iron, copper, etc., such as "kupfer-nickel" and "pyrrhotite." The experiments afforded such promising results that apparatus of considerable size, though still well within the limits of the resources of a laboratory, was set up, and in it several pounds of ore could be treated with carbon-monoxide.<sup>1</sup> A patent was also applied for on August 12, 1890, which describes the way in which such ores may be treated. It is pointed out that the principal nickel ores

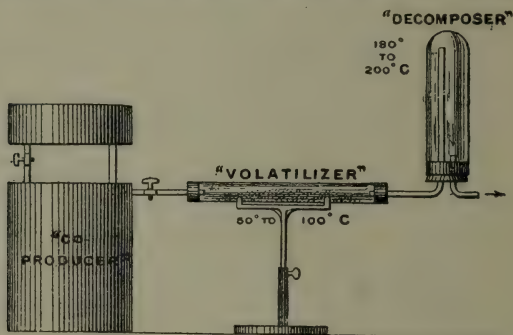


FIG. 188.

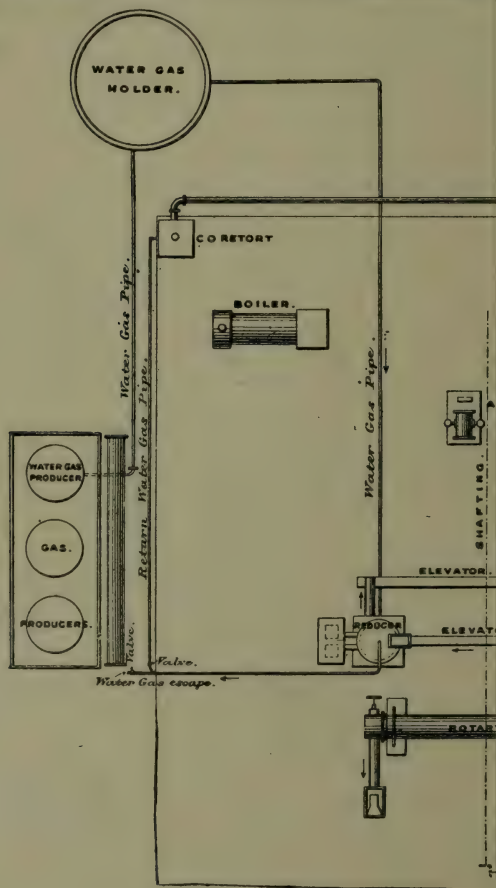
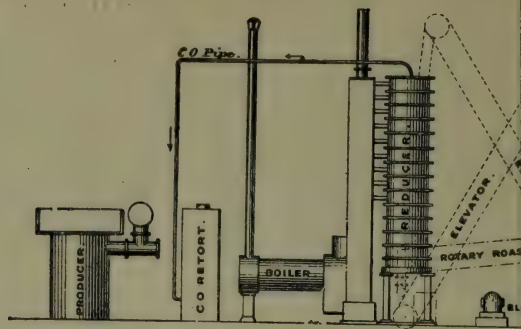
which are metallurgically treated contain the nickel in combination with arsenic and sulphur besides other metals and gangue. These ores have first to be submitted to the process of calcination, in order that the nickel may be present in the form of oxide, and to drive off, as far as is practicable, the arsenic, sulphur, and other volatile bodies. The resulting oxide of nickel is treated with reducing gases, such as water-gas or producer-gas, in order to convert the oxide of nickel into finely divided metallic nickel; the material containing it is then cooled to about 50° C., and is treated with carbon-monoxide. In dealing with nickel ores which contain nickel oxide in chemical combination with silicic acid, arsenic acid, or other substances which cannot be removed by calcination, the ores are so treated as to convert the nickel into nickel speise or nickel matte, which is then subjected to calcination. The actual experiment upon which the beautiful process is based may be indicated by a diagram, fig. 188. The gasholder

<sup>1</sup> Ludwig Mond on "Metallic Carbonyls," *Proc. Roy. Inst.*, vol. xiii. p. 668.

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*Introduction to Metallurgy.]*





contains carbonic oxide, and a little of the gas is ignited to show that it burns with the characteristic flame of that gas. The gas then passes over finely divided metallic nickel at a temperature not necessarily exceeding  $50^{\circ}$  C., and the luminosity of the flame is materially increased. In a very few minutes the carbonic monoxide will take up its charge of nickel, and a luminous flame will deposit its nickel on any cold surface held over it. It can thus be shown within what a very small range of temperature the whole operation is conducted. By passing the gas into a tube, and by heating it, a brilliant deposit of metallic nickel is obtained on the inside, in the form of a mirror.

In 1892 an experimental plant on a large scale was erected at Smethwick, near Birmingham. After some years of patient work, during which the plant had several times to be reconstructed, in order to meet all the conditions of this somewhat delicate process, it gradually assumed the shape shown in fig. 189. Before describing it in detail, it will be well to give a brief account of the operations involved in the process, which are the outcome of many years' practical experience.

The process is more especially suitable for the extraction of nickel from ores which contain copper in addition to nickel and iron. These ores, which have on an average between 2 per cent. and 6 per cent. of nickel and about the same amount of copper, are first subjected to "heap roasting," to eliminate the greater part of the sulphur, and to convert the iron, which forms their chief constituent, into oxide. The roasting is necessary to enable the iron in the following operation of smelting to combine with the silica present in the ore to form a slag, and thus to effect the separation of the iron from the nickel and copper which unite with the remainder of the sulphur to form a regulus or matte. This matte contains the nickel and copper in a more concentrated form, the amount of each metal being usually 15 per cent. to 20 per cent., the residue consisting mainly of sulphur and iron. To concentrate the nickel and copper still further, the matte is "Bessemerised." A sample of such "Bessemerised" matte contained 31.37 per cent. of nickel, 48.62 per cent. of copper, and 0.70 per cent. of iron. It was prepared by the Canadian Copper Company, Sudbury, Ontario, from their ores, which contain an average of 4 per cent. of nickel and 4 per cent. of copper. This "Bessemerised" matte is crushed, ground, and subjected to a calcining operation so as to convert the sulphides into oxides, and it is then passed through a mill and dresser. This calcined Bessemer matte then consists practically of nickel oxide and copper oxide in varying quantities. It has been found in the practical working of the process to be advantageous to further concentrate the nickel by extracting part of the copper at this stage by treating the mixtures of oxides with dilute sulphuric

acid, which dissolves about two-fifths of the copper present with-

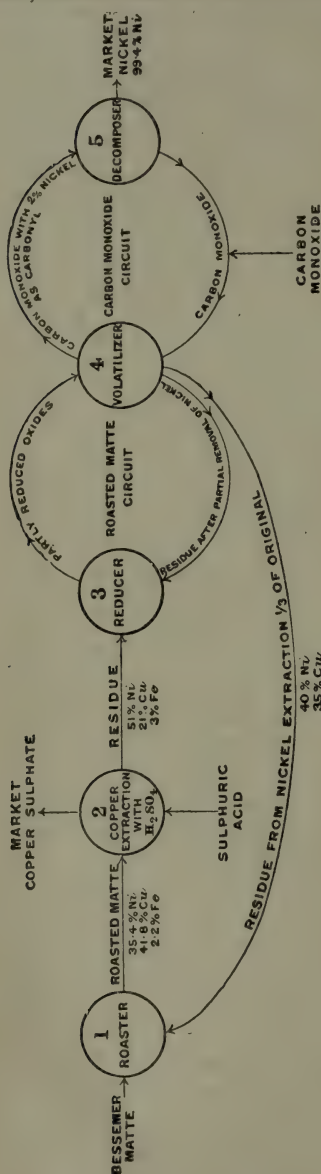


Fig. 190. — Diagram illustrating the Five Operations involved in the Mond Process.

out taking up more than 1 per cent. to 2 per cent. of the nickel. The copper thus dissolved is in the form of copper sulphate and is obtained in a marketable form by crystallisation. The undissolved residue from this operation contains between 45 per cent. and 60 per cent. of nickel, and, after drying, it is subjected to a carefully regulated reducing process by means of water-gas, after which it is treated with carbon-monoxide to extract part of the nickel present. In this first treatment with carbon-monoxide about two-thirds of the nickel can be easily extracted; after this amount is volatilised the extraction becomes much slower, so that it has been found advantageous to recalcine the residues and repeat the copper extraction, the reduction, and the nickel extraction.

The five operations involved are diagrammatically illustrated in fig. 190. The process begins, as will be seen, at one end with the material to be treated, "Bessemerised" matte; it ends with the market product, nickel. The "Bessemerised" matte proceeds, as the arrow indicates, to the first operation (1) of dead roasting, and for this purpose any suitable

furnace may be employed. After roasting, the matte contains

35 per cent. of nickel, 42 per cent. of copper, and about 2 per cent. of iron.<sup>1</sup> It then passes to the second operation (2) for the extraction of part of the copper (about two-thirds) by sulphuric acid, the copper being sold as crystallised sulphate of copper. The residue from this process contains about 51 per cent. of nickel and 21 per cent. of copper, and passes to the third operation (3) for reducing the nickel and incidentally the remaining copper, to the metallic state, care being taken to avoid reducing the iron. This is effected in a tower provided with shelves, over which mechanical rabbles pass, the reducing agent being the hydrogen contained in water-gas. The temperature does not exceed 300° C., and should be kept lower when much iron is present. From this tower the ore is conveyed continuously to the fourth operation (4) of volatilisation, in which part of the nickel is taken away by carbon-monoxide and forms the compound nickel carbonyl. The formation of this volatile compound is effected in a tower similar to the reducing tower, but the temperature is much lower, and does not exceed 100° C. From the volatiliser, the ore is returned to the reducer (3), and it continues to circulate between stages (3) and (4) for a period varying between seven days and fifteen days, until about 60 per cent. of the nickel has been removed as nickel carbonyl. The residue from this operation, amounting to about one-third of the original calcined matte, and not differing much from it in composition, is returned to the first operation and then naturally follows the same course as before. The nickel carbonyl produced in the fourth operation passes to the decomposer. This appliance is either a tower or a horizontal retort, which is heated to a temperature of 180° C., so as to decompose the nickel carbonyl and release the nickel in the metallic form, either on thin sheets of iron or, preferably, on granules of ordinary commercial nickel. Carbon-monoxide is also released, and is returned to the volatiliser to take up a fresh charge of nickel. It will be evident that when the operation is in progress, the gaseous carbon-monoxide and the partially reduced oxides of nickel and copper are continuously revolving in two separate circuits which join and cross each other in the volatiliser. The commercial product contains between 99.4 per cent. and 99.8 per cent. of nickel.

It will now be possible to proceed to a description of the working as the author saw it in full operation during a visit to Smethwick. The material under treatment during the author's visit was of Canadian origin, and had been received as calcined Bessemer matte containing 35.4 per cent. of nickel, 41.8 per cent. of copper, and about 2 per cent. of iron. This material was first passed through a ball mill and dresser with a 60-mesh riddle,

<sup>1</sup> Average results are given in the figure rather than the best which have been obtained.



and was then treated in quantities of 3 cwt. in a small lead-lined mixer with 200 lbs. of ordinary sulphuric acid, which had previously been diluted with about 20 cubic feet of mother liquor from previous operations. The temperature of the mixture soon rises by the action between the copper oxide and the sulphuric acid, and is kept, by means of a steam-jet, at a temperature of about 85° C. for half an hour. From this mixer, the charge is run out into a centrifugal hydro-extractor, provided with a filtering cloth, in which the solution of copper sulphate is separated from the solid residue containing the nickel. After the filtration of the charge is finished, the speed of the hydro-extractor is increased, and the residue is thus rendered sufficiently free from the liquor.

The solution containing the extracted copper runs from the hydro-extractor into a well, from which it is pumped into the crystallising vats. After a period of about eight days to ten days, the crystals of copper sulphate are taken out of the vats and the mother liquor is mixed with fresh acid and is again used for the extraction of copper. As already mentioned, a small amount of nickel and a little iron are also dissolved in the sulphuric acid during the copper extraction, so that the mother liquor from which the copper sulphate has crystallised becomes gradually contaminated with these two metals. It is therefore necessary to replace some of the mother liquor from time to time by fresh water, and to recover the nickel from the solution. The simplest method is to evaporate the solution to dryness and to roast the nickel and copper sulphates so obtained. The oxidised material is again introduced into the main process. The copper sulphate crystals from the crystallising vats are charged into a second hydro-extractor, where they are washed with a little clean water to remove all acidity; they are then dried and are ready for packing. The copper sulphate thus obtained is sufficiently pure for the market, as it contains only 0.05 per cent. of nickel and 0.048 per cent. of iron.

The residue from the copper extraction is taken from the hydro-extractor and stored in a bin until a sufficient quantity has been collected to make up a charge of 5 tons to 6 tons for the nickel-extracting plant. It now contains 52.5 per cent. of nickel, 20.6 per cent. of copper, and 2.6 per cent. of iron. The material is charged by hand at the rate of  $\frac{1}{2}$  ton per hour into a feeding-hopper, which communicates, through a rotary valve, with the conveyor, consisting of a tube enclosing a revolving spiral, which transports the material to an elevator. This lifts the material to the top of the reducing-tower, and discharges it through another rotary valve into this reducing-tower.

The reducer and the volatiliser in which the treatment with carbon-monoxide takes place, are fully described in Dr Mond's patent (No. 23,665 of December 10, 1895). The reducer consists of a vertical tower about 25 feet high, containing a series of



shelves, which are hollow so as to admit of their being raised to a temperature of  $350^{\circ}$  C. by producer gas. The roasted matte falling on these shelves from above is stirred and made to descend from one shelf to that below it by rabbles actuated by a central vertical shaft. Water-gas passes up the tower to effect the reduction of the material. There are about fourteen of these shelves or trays in the tower. The five lower shelves are not heated by producer gas, but are cooled by a stream of water in order to reduce the temperature of the roasted and reduced matte to the temperature at which the volatiliser is worked.

The volatilising-tower resembles the reducer, but the shelves are not hollow, as there is no necessity to heat them. The reduced nickel requires a temperature of only  $50^{\circ}$  C. to enable it to combine with carbon-monoxide and form a volatile compound, and the material and gas are sufficiently hot to maintain this temperature. In the plant at Smethwick the volatiliser was made the same size as the reducer, but in the new plant it is somewhat smaller.

The decomposer has been devised with much care, and the nickel is deposited in it, from its gaseous compound with carbon-monoxide, on granules of ordinary commercial metal. The arrangements by which this is effected are very ingenious, and may be described almost in the words of Dr Mond's patent. The object is to obtain metallic nickel from nickel carbonyl in the form of pellets, which are specially suitable for the production of nickel alloys. For this purpose gases containing nickel carbonyl are passed through granulated nickel, which is kept at the temperature required for the decomposition of the carbonyl—about  $200^{\circ}$  C. The nickel which thus separates from the carbonyl becomes deposited on the granulated nickel, which consequently increases in size. In order to prevent cohesion of the granulated nickel, it is kept in motion. When a number of the pellets have attained a convenient size, they are separated by sifting without interrupting the depositing operation, the smaller granules being returned to receive a further deposit from the nickel carbonyl. The appliance used for depositing the nickel originally consisted of a series of retorts lined with thin steel sheets, on which the nickel was deposited in layers. It was found, however, that the metal so obtained was very difficult to cut, and the apparatus above described was accordingly devised.

A magnified section of a granule of nickel, about  $\frac{3}{4}$  inch in diameter, shows a core of nickel which under higher magnification appears as a crystalline and convoluted structure, and this core is surrounded by concentric layers. The central core is ordinary commercial nickel, and the layers are nickel deposited from its carbonyl. In some cases granules of deposited nickel are found without any central core. These have grown from minute frag-

ments of deposited nickel which have become detached during the course of deposition.

The water-gas used in the reducer is generated in gas-producers ; anthracite is used to decompose the steam, and the water-gas is collected in a gas-holder, whence it is taken to the reducing-tower, to which reference has just been made. This gas contains, on entering the reducer, about 60 per cent. of hydrogen.

The reducing operation is so regulated that only a small quantity of hydrogen remains in the escaping gas, as a rule not more than 5 per cent. to 10 per cent. This waste gas is subjected to the action of a fine water-spray, which condenses the steam generated by the combustion of the hydrogen in the water-gas. Part of this waste gas is used for making the carbon-monoxide required in the volatiliser, by passing it through the CO retort charged with incandescent charcoal, which reduces the carbon-dioxide contained in the waste gas, and this increases the amount of carbon-monoxide in it. The gas issuing from this retort contains about 80 per cent. of carbon-monoxide, and is stored in another gasholder, which communicates with the main circuit of the carbon-monoxide gas. This main circuit of the carbon-monoxide passes through the volatiliser already referred to, where the nickel is taken up. The carbon-monoxide, now charged with nickel, passes through a filter to separate the fine particles of matte-dust from the gases, then through an apparatus called the decomposer, and so described in the figure. In this decomposer the nickel taken up in the volatiliser is deposited. The gas, now deprived of its nickel, passes to the CO blower, which sends the carbon-monoxide to the volatiliser in order that it may take up a fresh charge of nickel.

The solid material from which the nickel is being extracted is kept circulating through the reducer and volatiliser for a period varying between seven days and fifteen days, during which time the oxides are gradually reduced to the metallic state and the nickel volatilised. When the material originally charged in has had the bulk of its nickel extracted it is run out through a rotary calciner, which converts the metals into oxides, so that they may be treated for the second time with sulphuric acid and carbon-monoxide. The ratio between the nickel and copper in the residues from the nickel extraction is practically the same as in the calcined Bessemer matte, with which the operations were started, but the amount of iron has increased by the removal of the copper and nickel, as the following figures show :—Original matte contains, nickel, 35·27 per cent., copper, 41·87 per cent., iron, 2·13 per cent. After the first treatment of copper and nickel extraction, the quantities are, nickel, 35·48 per cent., copper, 38·63 per cent., iron, 4·58 per cent. ; and, after the second copper and nickel extraction, nickel, 35·83 per cent., copper, 35·56 per cent., and iron, 7·82 per cent. The amount of nickel extracted

in these two cases was, after the first treatment 61 per cent., and after the second treatment 80 per cent. of the nickel present in the original matte. It must be remembered, however, that in the second treatment only one-third of the original amount remains to be treated, while the final residue is only one-tenth. To avoid the formation of iron carbonyl, the temperature in the reducer has to be kept very low, and if this is done, the nickel extracted from a matte originally containing as much as between 6 per cent. and 10 per cent. of iron will not contain more than 0·5 per cent. of iron. If the amount of iron in the residues rises above this percentage, the extraction of the nickel is very much delayed, on account of the low temperature which must be maintained in the reducer. It is necessary, in such a case, to re-smelt the residues before proceeding with the extraction of the nickel and copper. The following are analyses of the deposited nickel:—

	I.	II.
	Per cent.	Per cent.
Nickel . . . . .	99·82	99·43
Iron and ( $\text{Al}_2\text{O}_3$ ) . . . .	0·10	0·43
Sulphur . . . . .	0·0068	0·0099
Carbon . . . . .	0·07	0·087
Insoluble residue . . . .	...	0·026

By the kindness of Dr Mond, the author is able to indicate the nature of the plans required for a large manufacturing plant. This plant will, it is estimated, produce 1000 tons of nickel per year. The plant is so arranged that the matte is continuously charged into the first reducer and traverses the whole set of appliances. When the matte issues from the last volatiliser the nickel extraction is finished. The matte is re-roasted and submitted to the second copper and nickel extraction. There are ten appliances, consisting of one large reducer, eight combined reducers and volatilisers, and one large volatiliser. They are so arranged that the matte has first to pass through the large reducer, and is then lifted, by means of an elevator and conveyor, into a volatiliser (erected on the top of the next reducer). It passes through the volatiliser into the upper portion of the reducer, and in traversing this it is further reduced. It is then lifted again to the next volatiliser, and so on till it finally reaches the larger volatiliser at the end of the whole series, and, after passing through this, it is discharged into the roasting-furnace. The conveyor on the top of the volatilisers into which the elevators discharge, is common to the whole set of volatilisers and reducers, so that, in case any portion of the plant has to be disconnected, the rotary valve through which the material is discharged from



the conveyor into the volatiliser is stopped. The material then passes on through the conveyor into the next volatiliser. The two gases, carbon-monoxide in the volatilisers and water-gas in the reducers, are kept separate by rotary valves of the same construction as in the small plant. The water-gas connections are so arranged that each reducer receives fresh gas from the main, with the exception of the first large reducer, through which the waste gas of all the other reducers is passed, so as to burn completely all the hydrogen in the water-gas. The carbon-monoxide passes through the volatilisers from a common main, and is collected, after it has passed through the filters, in a main leading to the blower. From the blower the carbon-monoxide charged with nickel passes through a set of decomposers, and again into the main which feeds the volatilisers.

The Mond Nickel Company, Limited, of Clydach (Glamorgan), who have acquired Dr Mond's patents, have erected two large units as above described, which have now been in successful operation for about five years.

With regard to the application of steel containing between 1 per cent. and 7 per cent. of nickel in constructive work, it is not necessary to insist upon the importance of nickel steel not only for the manufacture of armour-plates but for all purposes where strength and lightness are essential. One manufacturer in the United States used in one year no less than 178 tons of nickel in the form of nickel steel, and it has been stated by a competent authority that "if propellor shafts were made of nickel steel the question of failures would seldom or never be raised." An attempt to deal adequately with the application of nickel would lead far beyond the scope of the present work, and the author only adds that the extraordinary properties of these alloys have formed the subject of elaborate investigations by the late Dr John Hopkinson<sup>1</sup> and by Mr Guillaume.<sup>2</sup>

Since the above description was written, the use of nickel for coinage (in some sixty countries), for cooking and other domestic utensils, and in nickel steel, has very largely augmented, especially the use of the latter in armour-plates, artillery, shafts and axles, steel rails, and bridge-building.

It will have been evident that the process possesses unusual interest as being the only one, in the whole range of metallurgy, in which a metal is obtained from its ores by causing it to combine with a gas to form a gaseous product from which it is subsequently released. Not the least remarkable feature of the process is presented by the fact that the temperature at which the whole operation is conducted never exceeds 350° C., which is far below dull redness. As a consequence, the plant is not, as is usually the case with metallurgical appliances, subjected to altera-

<sup>1</sup> *Proc. Roy. Soc.*, vol. xlvii. p. 23 ; vol. xlvii. p. 138 ; vol. xlviii. p. 1.

<sup>2</sup> *Comptes Rendus*, vol. cxxiv. pp. 176, 752, and 1515, and vol. cxxv. p. 235.



tions of temperature extending through a considerable range. The repairs needed are therefore inconsiderable, and the amount of fuel required is but small. The process works more or less automatically, and the amount of labour involved in conducting it can be reduced within very narrow limits. The main operation is, moreover, a regenerative one; the carbon-monoxide moves in a cycle and is the vehicle for continuously transferring the nickel from the ore or matte, and converting it into a marketable form. It follows that in the extraction of the nickel no new material except the reducing agent, water-gas, has to be introduced into the system. This is true even of the granules of commercial nickel which fill the decomposer and serve as a basis for the deposition of the nickel from the carbonyl. Their presence is essential in starting the process; but their place is, as has already been pointed out, gradually taken by fragments of the deposited metal which become detached as the operation proceeds. The process will always occupy a prominent place in chemical history, and there would seem to be no reason why it should not play an important part in metallurgical practice.

**Separation of Nickel and Copper by Means of Sodium Sulphide.**—This process is applicable to the treatment of matte containing nickel, copper, and iron, and in it advantage is taken of the power which sodium sulphide possesses of dissolving sulphides of copper and iron, forming a solution of lower specific gravity than nickel sulphide.

In its original form the process consisted of mixing the matte with sodium sulphate and coke, running through a cupola, in which the sodium sulphate is reduced to sulphide, and allowing the molten product to flow into moulds, and separate, according to the specific gravity of the two portions. The different portions were then separated by fracture, and the tops, containing sulphides of copper, iron, and sodium, were charged into a smelting-furnace where the sodium sulphide was fluxed off in an iron slag and lost. The bottoms, containing nickel with some copper and iron, were re-treated with sodium sulphate and carbon, four or five treatments being necessary before the nickel was ready for reduction and purification.

In a modification of the process, the matte is so smelted that it will remain in a molten state subject to the high temperature of the furnace for a considerable time, during which the copper and iron sulphides are thoroughly dissolved by the sodium sulphide, and a good separation can be obtained in one melting. An open-hearth reverberatory furnace is used, lined with magnesite brick, and the matte is charged either solid or molten with 60 per cent. of its weight of sodium sulphate, and 15 per cent. of coke.

A 50-ton charge is kept molten for four or five hours after fusion, during which time it is kept poled with poles of green wood. The charge may be run into moulds; but, in order to get

the best results, the different strata in the furnace are tapped separately, the lower strata of nickel sulphide being tapped first. The nickel sulphide thus obtained is nearly pure, but when greater purity is required, it is recharged into the same furnace and re-treated.

**The Electrolytic Refining of Base Bullion—Bett's Process.<sup>1</sup>**  
—The refining of base bullion, argentiferous lead, etc., by means of Bett's process is becoming of considerable importance. The plant consists of wooden electrolysing vats coated with rubber paint, and has the general arrangement of a copper-refining plant.

The electrolyte consists of an acid aqueous solution of lead fluosilicide containing 8 per cent. of lead and 15 per cent. of free hydrofluoric acid. To this solution a certain addition of gelatine is added (about 0.1 gramme per litre), in order to make the deposit smooth and dense, for without this addition the cathode deposit is found to lack solidity and branches of the metal grow towards the anode and cause short-circuiting.

The electrolyte is made by diluting hydrofluoric acid (35 per cent.) with an equal volume of water, saturating with pulverised quartz, and then treating with white lead in the proper quantity, filtering, and adding the necessary gelatine or glue. In one plant the vats are 86" × 30" × 42" deep; they hold 22 anodes weighing 3 tons.

The cathodes consist of thin sheets of pure lead suspended from copper bars. The electrodes are placed at a distance of 1½ to 2 inches. In a tank through which 4000 ampères are passing, 750 lbs. of refined lead are deposited per day.

During the process, Au, Ag, Cu, Sb, As, and Bi go into the anode mud, while Sn, Fe, Zn, Ni, and Co go into solution.

After the solution in the electrolysing vats has been in use some time it becomes contaminated with impurities and requires purification. For this purpose the lead present is first precipitated by means of sulphuric acid, and the hydrofluoric acid is precipitated by means of sodium chloride as sodium fluosilicate; from this compound the hydrofluoric acid is recovered with one-third the sulphuric acid required to decompose calcium fluoride.

The slimes may contain 8000 ounces of silver-gold per ton and are treated by the following process<sup>2</sup>:—

1. The slime is agitated by means of steam and air in a lead-lined tank with ferric sulphate solution; this sulphatises the copper, lead, and silver, dissolves all the copper and some silver, converts arsenic, antimony, and bismuth into oxides, and forms ferrous sulphate and free sulphuric acid.

2. The solution from No. 1 is treated with metallic copper in order to precipitate the silver.

<sup>1</sup> *Mineral Industry*, 1905, p. 421; *Zeit. für Electrochemie*, 1905, xi. p. 229; *Mines and Minerals*, 1905, xxv. p. 285.

<sup>2</sup> A. G. Bett's *Electrochemical and Metallurgical Industry*, 1905, iii. p. 272.

3. The residues from 1 and 2 are filter-pressed, washed, and then agitated with solution containing 12 to 15 per cent. hydrofluoric acid and 2 to 4 per cent. sulphuric acid to dissolve the antimony.

4. The residues from 3 are melted with soda and parted electrolytically, using an electrolyte containing 15 per cent. methylsulphuric acid, 7.5 per cent. of silver, and a gelatine addition equal to 1 part in 12,000. As a result of this electrolysis pure silver is obtained, any gold is retained in the linen bag in which the anode is placed, and copper and bismuth pass into solution. This solution is first treated with copper to precipitate any silver it contains, then the copper and bismuth are removed with lead. The bismuth and copper are separated by means of ferric sulphate, and the bismuth oxide thus obtained is reduced.

5. Copper oxide is added to the solution from 4, arsenic crystallised out, if necessary, then the solution is electrolysed, carbon anodes being used ; ferric sulphate is thus regenerated and is returned for use in operation 1.

6. The antimony fluoride solution from 3 is electrolysed, regenerating hydrofluoric acid to be used again in 3.

## CHAPTER XIII.

### ECONOMIC CONSIDERATIONS.

**Object of the Metallurgist.**—Viewed in its commercial aspect, the object of the metallurgist is to render science subservient to manufacturing art, or what is equivalent, to make science remunerative. If, as has been well observed, we hope to urge on practical metallurgists the importance of combining scientific with practical knowledge, it must be demonstrated that the combination will be of pecuniary advantage to themselves, as they can have no inducement for investing capital to carry into practice an invention, however beautiful and attractive in a scientific point of view, apart from the consideration of gain. This being the case, it will be well for the student to bear in mind a few of the principles by which the relations of capital and labour are guided, and the economic conditions under which metallurgical works are carried on.

**Capital and Labour.**—In the early stages of the metallurgical art, when the metals were extracted from their ores either by the direct action of heat, or by the aid of simple reactions, man was, as Gruner shows, in a measure the sole mechanical agent in this industrial art; but when machines and appliances were devised, the agency of man became less apparent. In order to obtain these machines, capital is necessary, and capital has been defined as “accumulated work,” stored, that is, from some period anterior to that in which it has been brought into play. This accumulated work also demands payment when it is utilised, and this payment is the interest received by the capitalist who furnishes the equivalent of work. Manual labour is still necessary, and its influence is always considerable, even though it bears a less direct relation than formerly to the cost price of the product. It must be remembered, however, that there has always existed between capital and labour, between the employer and the employed, antagonism which it is very difficult to entirely banish. The utmost care should nevertheless be devoted to reducing it to the smallest possible limits, and, as the condition of operatives has materi-



ally improved during the last half-century, it is certain that the efforts that have been made on their behalf have not proved fruitless.

There is a widespread feeling that the interests of capital and labour must be antagonistic, and, as it is impossible to ignore the fact that the conflict between them is giving rise to grave apprehension, it becomes the duty of all who possess influence to strive not merely for peace, but to range themselves on the side of justice and humanity. The great labour question cannot be solved except by assuming as a principle that private ownership must be held inviolable, but it must be admitted that there was a time when capital had become arbitrary and some kind of united action on the part of workmen was needed in self-defence. If, however, we turn to the action of the leaders of trades unions in various lamentable strikes in the past, we are presented with a picture which many of us can only view as that of tyranny of the most close and oppressive kind, in which individual freedom cannot even be recognised. There are hundreds of owners of works who long to devote themselves to the true welfare of those they employ, but who can do little against the influence of the professional agitator, and are merely saddened by contact with prejudice and ignorance. The view is probably correct that some system by which the workman participates in the profits of enterprise will afford the most hope of putting an end to labour disputes, and we are told that profit-sharing tends to destroy the workman's sense of social exclusion from the capitalistic board, and contents him by elevating him from the precarious position of a hired labourer. No pains should therefore be spared in perfecting a system of profit-sharing.

Pensions are great aids to patience and fidelity. Watchful care over the health, interests, and instruction of the employed is exercised by many owners of works. Workmen must not forget that the choice of their own leaders is in their own hands, and on this the future mainly depends. "We may lay it down as a perpetual law that workmen's associations should be so organised and governed as to furnish the best and most suitable means for attaining what is aimed at, that is to say, for helping each individual member to better his condition to the utmost in body, mind, and property." The words will be found in an Encyclical letter which Pope Leo XIII. issued on the "Condition of Labour," and it is specially interesting that the Bishop of Rome, in his forcible appeal, again and again cites the opinion of St. Thomas Aquinas, who was a learned chemist as well as a theologian.

Those of us who realise that "the higher mysteries of being, if penetrable at all by human intellect, require other weapons than those of calculation and experiment," should be fully sensible of our individual responsibility. Seeing that the study of the

relations between capital and labour involves the consideration of the complex problems of existence, the solution of which is at present hidden from us, we shall feel with Andrew Lang that "where, as matter of science, we know nothing, we can only utter the message of our temperament." It is to be hoped that the patriotism of the masters and workmen will prevent them from driving our national industries from these shores, and those to whom the direction of the metallurgical works of this country is confided, may be asked to remember that we have to deal both with metals and with men, and have reason to be grateful to all who shall extend the boundaries, not only of our knowledge, but also of our sympathy.

The hope that workmen would not drive national industries from our shores was expressed in the author's address as President of the Chemical Section of the British Association in 1891, but it is to be feared that a warning is still greatly needed. In 1893, so trustworthy an authority as Sir Joseph Pease has addressed such a warning to *The Times*.<sup>1</sup> He says, "With peace between capital and labour we shall hold our own; with war, our trade will leave us. . . . A leading firm tell me," he adds, "that they are at this moment carrying out two lines of railways in British colonies and with British capital, but all the bridge work, steel sleepers, and rails come from Germany. At Aachen, some hours distant from the coast, thousands of tons of steel sleepers are being made for English companies; 30,000 tons of rolled joists were made at Halle, in Belgium, and used in London alone last year. The roof for the Athenæum in Liverpool, and that for the new United Service Institution at Whitehall, were manufactured abroad. And this is the case whilst there are multitudes at home who cannot get work at any price, and others are refusing it even on terms to be settled by arbitration."

It will be evident that some knowledge of political economy is absolutely necessary as an "Introduction to the Study of Metallurgy," and the author has written this in the earnest hope that the lesson that capital and labour must work together may not be learned too late.

**Modes of Payment.**—In metallurgical works piecework is the system generally adopted. This simply consists in paying the workmen, in proportion to the amount of work executed, at a settled rate. It is the only system that conduces both to the interest of the employer and the employed. The first and most considerable difficulty consists in fixing the price of the piece, or the unit of work, and the adjustment of the contract affords abundant opportunity for the exercise of forbearance and equity on the part of the employer. The arrangement is more complicated where, instead of agreeing with a single workman, it is

<sup>1</sup> *The Times*, October 6, 1893.

necessary to entrust work to several workmen associated as partners. It is then impossible to divide the work equally, for some of the workmen are more experienced than others. In this system it is also difficult to ensure that the work executed is of good quality, and careful supervision is necessary.

Remarkable results have been attained with this system at the Creusot, Terre Noire, and other French steelworks, where the wages have increased 50 to 60 per cent., and the production has been doubled in the space of a few years, and that without increasing the number of hours of work. A special stimulus, too, is given by progressive payments—that is to say, by increased payment for the supplementary tons in excess of the normal output of iron or steel.

The adoption of this system of giving premiums has been attended with marked success. At the great Belgian zinc-works of La Vieille Montagne, the smelters and mill men receive, in addition to a fixed wage, a premium calculated on the output, and a special premium is also given for unwonted energy. In some cases, the firemen receive a similar premium, based on the time their furnace lasts without repair. In other cases the workmen receive a premium when they obtain from the ores a greater amount of metal than that which they are calculated to yield. Two-thirds of this premium is paid periodically with the regular wage. The remaining third is retained until the end of the year, and it is not paid then unless the workmen have worked regularly throughout the year.

The majority of men in iron and steel works are paid per unit of work—that is to say, by the ton or quantity of work they turn out.

At the Royal Mint, London, a somewhat peculiar system is adopted. Prior to 1870, the workmen were paid on an average 2s. 8d. per 1000 accurately struck coins, and when the Mint was not at work they received a small payment amounting to from 6s. to 10s. per week. The objections to this system are obvious. When the department was in full work, the men received an average of £2, 15s. per week, and during the remainder of the year they received allowances insufficient to maintain them, or to prevent their forming other engagements. The result was, on the one hand, that the more improvident among them contracted liabilities and returned to work in debt, and, on the other hand, that the more skilful workmen were induced to accept employment elsewhere, and the Mint lost their services. The rate paid for piecework was therefore slightly reduced, and a uniform payment of £1 per week for the men, and 10s. to 15s. per week for the boys, as “subsistence money”—as it is termed—was set on foot.

There can be no doubt that the system of premiums renders it possible to retain the services of good workmen, as well as to



stimulate and encourage their intelligence. It is the best method of enabling them to share in the profits, and at the same time it indirectly augments those of the employer.

We now come to a question that has been discussed with much interest in recent years. Certain economists and philanthropists urge that it would entirely remove antagonism between capital and labour, if the operatives directly participated in the profits of an undertaking. Others contend that this sharing of profits, far from effecting a better understanding between capital and labour, would only give rise to further troubles. In one shape or another participation of profits has found a good deal of favour on the Continent, where many works have adopted it with generally very beneficial results to all parties concerned. This has notably been the case at the ironworks of Godin, at Guise, France.<sup>1</sup>

M. P. Leroy-Beaulieu, editor of *L'Économiste française*, states that the system of participation in profits, viewed as a general method of organising labour, is both deceptive and dangerous. It may be possible to admit superior workmen and foremen to participation in profits; but in this country, at least, workmen are not ready for the change. Everything goes well as long as the works are carried on at a profit; but in bad times discontent soon breaks out. The system is not viewed with favour by the workmen themselves. They are perfectly willing to share in the profits, but they object to be answerable for their share of loss, and are even reluctant to contribute to a reserve fund to cover the losses of future bad years. A workman cannot either wait for better times, or turn out products at a loss in order to retain his employment. Moreover, the final participation appears too remote; the workman cannot appreciate the relation that exists between his work and the annual profit.

Among the methods that have been adopted for giving the men a permanent interest in the works, the following may be enumerated :—

1. The method of paying over to the workmen a share in an annual cash bonus.

2. Retention of the share for an assigned period, in order ultimately to apply it, together with its accumulated interest, for the workmen's benefit.

3. An annual distribution of a portion of the workmen's share and an investment of the remainder. This third method is adopted at the La Vieille Montagne zinc-works, where the results have been found to be most beneficial, and have entirely prevented strikes.

Whatever method be adopted, no effort should be spared to induce the men to exercise the utmost care in the conduct of their ordinary occupations. To illustrate this, Mr Kenward, the

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1888, i. p. 102.



manager of Messrs Chance's works, near Birmingham, stated that in such an apparently routine occupation as superintending a machine punching holes in a metal plate, a thoroughly active workman could realise a surplus wage three times as great as that obtained, under identical conditions, by a less strenuous but not less skilful fellow-workman. With due care, a large amount of the waste that occurs in every trade could be avoided. In metallurgical industries, this waste is often apparent, and in some cases the dimensions of the scrap-heaps are a source of wonderment to foreigners who visit this country.

Those who are not engaged in active constructive work can form no adequate conception of the enormous waste caused by inaccurate or bad workmanship, and this is well shown by the fact to which attention has been directed by Mr R. Caird, of the well-known firm of engineers and shipbuilders at Greenock. He estimates that iron and steel to the value of £5,000,000 are annually wasted as "scantlings," or are employed in excess of actual requirements in shipbuilding, and he states that over £200,000 are spent per annum in propelling excessive and unnecessary material.

Quite apart from the methods of remunerating labour, much will depend upon the personal relations between employer and employed, and more especially upon the moral example set by the heads of the firm, and upon the amount of care and interest they display in providing for the wants of their people in the way of schools, gardens, savings banks, libraries, and hospitals. In this country the provision made in this respect at such works as Crewe, Elswick, and Dowlais deserves especial commendation. At Crewe there is a well-organised institute, in which competent teachers prepare the younger operatives for the various technological examinations. Similar institutes have been founded at many other works.

No doubt where, as in the Royal Mint and other Government establishments, pensions can be given, they afford the most powerful inducements to industry and fidelity.

It is not necessary here to dwell upon the importance of technical education. The advantages that craftsmanship constantly reaps from scientific knowledge are standing proofs of the necessity for special training. All may be summed up in a few words borrowed from the writings of a former French Minister of Finance, Jules Simon:—

"The practised eye and the sure hand are much, but they do not replace Science. The smith who knows the drawbacks of too rapid oxidation, who knows why throwing water on the surface of fuel increases the heat at the centre of the mass, the puddler who takes into account the effect of an oxidising or reducing flame, and who exposes metals to one or the other at the right moment --such are evidently the best workmen, more skilful for current

needs, less disconcerted by an accident, less embarrassed by having to describe an observation, less slaves to routine, and quicker to adopt new processes." He points to the fact that so many of the modern inventions are due to workmen, and justly urges that the more intelligent the workman becomes, the better he will understand the skill possessed by those who direct him, and the more he will appreciate work that differs from his own.

In spite of all the advantages that technical education offers, it must be remembered that many metallurgical works in this country are successfully conducted by so-called practical men; not the kind of man so forcibly described by Sir Frederick Bramwell,<sup>1</sup> as one "whose wisdom consists in standing by, seeing, but not investigating, the new discoveries which are taking place around him, the aim and object of such a man being to ensure that he should never make a mistake by embarking his capital or his time in that which has not been proved by men of large hearts and large intelligence"; nor the man who accepts no rule but the rule of thumb, but practical men possessing technical knowledge of a high order, whose careful observations enable them to use the results of past experience in dealing with circumstances and conditions analogous to those they have met with before, and with which long practice has made them familiar. It would be difficult to overrate the value and importance of such knowledge as theirs, and, when we remember the scale on which smelting operations are carried on, it will be obvious that this kind of knowledge can only be gained in the works, and not in the laboratory or lecture-room, for, however careful metallurgical teaching in a school may be, it is only practical in a limited sense. At the same time, it must be borne in mind that a man trained to scientific methods starts with the enormous advantage of being able to deal with circumstances and conditions that are new to him, and with which, therefore, he cannot be said to be familiar. The technical skill that time and opportunity can alone give him will then rest on a solid basis. It is necessary, however, to guard against undervaluing the teaching of experience unaided by reasoning that we should recognise as scientific, for it is only necessary to witness such operations as the roasting of a large mass of ore on the bed of a furnace, or the forging of many tons of iron under a steam hammer, to appreciate the value of the subtle skill of sight and touch on which success depends.

The relation between scientific and technical men is thus traced, as hitherto there have been misunderstandings on both sides, or, as Dr Williamson<sup>2</sup> well observed, "Men of detail do not sufficiently appreciate the value or usefulness of ideas or of general principles; and men of science, who learn to understand and control things more and more by the aid of the laws of

<sup>1</sup> *Brit. Assoc. Rep.*, 1872, p. 238.

<sup>2</sup> Inaugural Lecture, University College, London, 1870.

Nature, are apt to expect that all improvements will result from the development and extension of their scientific methods of research, and not to do justice to the empirical considerations of practical expediency which are so essential to the realisation of industrial success in the imperfect state of our scientific knowledge."

While it is no longer necessary to justify the scientific teaching of metallurgy, it is as important as ever that the true relation of theory and practice should be clearly understood. It rarely happens that a process can be transferred from the laboratory to the works without important modifications; and it must be remembered that metallurgy is a manufacturing art, and that, when the truth of a theory has been demonstrated, a dividend has to be earned. This would, indeed, often be difficult without the aid of the practical man. Practical men have, however, ceased to undervalue science, and the most practical body of men in the world, in the best sense of the term, the ironmasters of this country, on whom its prosperity so largely depends, formed themselves, in 1870, into an Iron and Steel Institute, of which many of the members possess high scientific attainments, and are distinguished for scientific research.

Turn, then, to the advice given by those who were accustomed to deal with metals on a large scale. In 1873 Sir Lowthian Bell<sup>1</sup> stated: "If we would avoid the failure of what may be designated unscientific practice, or the failure of impracticable science, we must seek to combine commercial intelligence with a knowledge of those natural laws which form the only trustworthy groundwork of the complicated processes in which we are engaged."

Again, Sir W. Siemens,<sup>2</sup> in 1877, said, "It is not many years since practical knowledge was regarded as the one thing requisite in an iron smelter, whilst theoretical knowledge of the chemical and mechanical principles involved in the operations was viewed with considerable suspicion."

As regards the preliminary training in metallurgy, the utmost efforts of the student should be devoted to securing a thorough acquaintance with scientific methods and metallurgical principles, and at the same time, to gathering as many well-ascertained facts as possible, remembering that applied science is nothing but the application of pure science to particular classes of problems. It consists of deductions from the general principles, established by reasoning and observation, which constitute pure science. No one can safely make these deductions until he has a firm grasp of the principles, and he can obtain that grasp only by personal experience of the processes of observation and of reasoning on which they are founded.

<sup>1</sup> *Journ. Iron and Steel Inst.*, 1873, p. 12.

<sup>2</sup> *Ibid.*, 1877, p. 7.



**Production of Metals.**—According to a diagram prepared by order of the French Minister of Public Works, and shown at the Paris Exhibition of 1889, the world's production of metals in 1887 was as follows :—

	Quantity. Tons.	Value. Francs.
Pig-iron . . . . .	22,721,000	1,155,297,000
Silver . . . . .	3,383	700,500,000
Gold . . . . .	158	629,600,000
Copper . . . . .	291,000	324,908,000
Lead . . . . .	474,000	180,785,000
Zinc . . . . .	333,000	129,795,000
Tin . . . . .	35,000	95,123,000
Mercury . . . . .	3,794	19,780,000

The world's production of coal during the same year amounted to 435,024,000 tons, valued at 3,000,652,000 francs.

Since this table was compiled, an enormous increase in the production of metals has occurred, and the figures given for the year 1907<sup>1</sup> are as follows :—

Pig-iron . . . . .	60,680,014 metric tons.
Steel . . . . .	51,183,340 „
Silver . . . . .	193,542,381 troy ounces.
Gold . . . . .	19,958,764 „
Copper . . . . .	723,807 metric tons.

**Price of Metals.**—In an able paper,<sup>2</sup> published in 1887, Dr W. A. Wells contends that depression in trade is largely the result of depression in the prices of metals and other metallurgical products. It is interesting, therefore, to consider past experience in the production and price of metals.

In the case of iron Sir Lowthian Bell fixed the world's production of pig-iron in 1870 at 11,565,000 tons, which increased to 14,345,000 tons in 1872. From that date production remained stationary until 1879, when it was 14,048,000 tons. After 1879 the average make for the ensuing five years was 18,000,000 tons, and in 1883 it rose to 21,063,000 tons, or nearly 50 per cent. more than it was in 1879. In 1900 the world's production was considerably over 40 million tons, and in 1907 it was over 60 million tons. While the production of iron increased in the United Kingdom at the rate of 131 per cent. from 1870 to 1884, the increase in the production of the rest of the world during the same period had been 237 per cent.

Under such circumstances the price of pig-iron throughout the world has rapidly declined.

In America, pig-iron was 45 dollars per ton in 1870 ; in 1885 it was 16 dollars. Cleveland pig-iron was £4, 17s. per ton in 1872,

<sup>1</sup> *The Mineral Industry*, vol. xvi., 1908.

<sup>2</sup> *Contemporary Review*, 1887, p. 523.



£2, 10s. in 1880, 37s. 2d. in 1887, and 36s. in December 1893; while at the present time (May 1910) it is about 50s., Scotch pig-iron being 56s. In 1874 Bessemer steel rails were £12 per ton; in 1887 they were £4. Since 1870 there has been a marked increase in production on the same expenditure in capital and labour. In Great Britain, the yield of iron per workman per year was 173 tons in 1870, 194 tons in 1880, and 261 tons in 1884. During the period under consideration, there has been a large substitution of steel for iron. A ship of 1700 tons requires 17 per cent. less material if made of steel than if of wrought iron; at the same time its efficiency is 7 per cent. greater in the former case. Again, on account of the greater durability of steel, a rail of this material has a life probably three times as long as that of an iron one. The same period has witnessed a great diminution in the production of puddled iron. This, it has been computed, resulted, in the ten years from 1875 to 1885, in the loss of £4,667,000 of capital invested in puddling-furnaces in England alone.

Other metals have also undergone great fluctuations in price; in most cases there has been a decline. In the case of copper, the increased annual production for the year 1885, compared with 1873, was 97 per cent., the increase being chiefly in the United States, Spain, and Portugal. In 1886 copper reached its lowest price, it having been, at New York,  $9\frac{1}{2}$  cents. per lb., whilst in 1880 it was 25 cents per lb. In January 1887, Chili bars cost £40 per ton. Many mines had to stop working, for at such prices they could only work at a loss. The great mines alone kept on, but their dividends were considerably reduced. This state of things led to speculation in copper, and endeavours were made to buy up a certain quantity of this metal, to raise the price, and then to sell at a profit. A syndicate was formed in Paris, and large quantities of copper were bought. The first results exceeded all expectations. Copper rose in a short time from £40 to £80. It was then resolved to make the affair permanent, and the syndicate contracted with the leading copper mines to buy their output at a given price. It undertook, in fact, to take 150,000 tons a year, involving an outlay of at least £9,000,000. Besides this, in order to keep up the price and the monopoly, it was necessary for the syndicate to buy all the output of those mines which declined to contract. One of the chief factors in the affair, however, was overlooked. Consumers did not come forward as in previous years. Copper came into the market from all directions, and, owing to the high prices, old sheathing was melted down, meeting the consumption, and copper in many cases was superseded by iron or steel. In short, the stock of the syndicate swelled daily in alarming proportions, and in February 1889 the crash came, and copper fell to £39. Since this date it steadily rose, until August 1890, when it was £60 per ton. In August

1897 the price of copper was £51 per ton, while in April 1899 it reached the high figure of £78, after which it fell, and during December 1902 the average price was £51. After this a gradual rise again took place, and in February 1907 the price reached £107, 5s., from which figure it has gradually fallen again and is now (May 1910) £56 per ton.

From 1880 to 1885, the world's production of lead increased about 30 per cent., and the price fell in the same proportion. In the latter year, there was great commercial distress among British lead miners and smelters. The price in August 1897 was about £13 per ton, in July 1907 over £20, whilst at the present time (May 1910) it is £12, 10s. per ton.

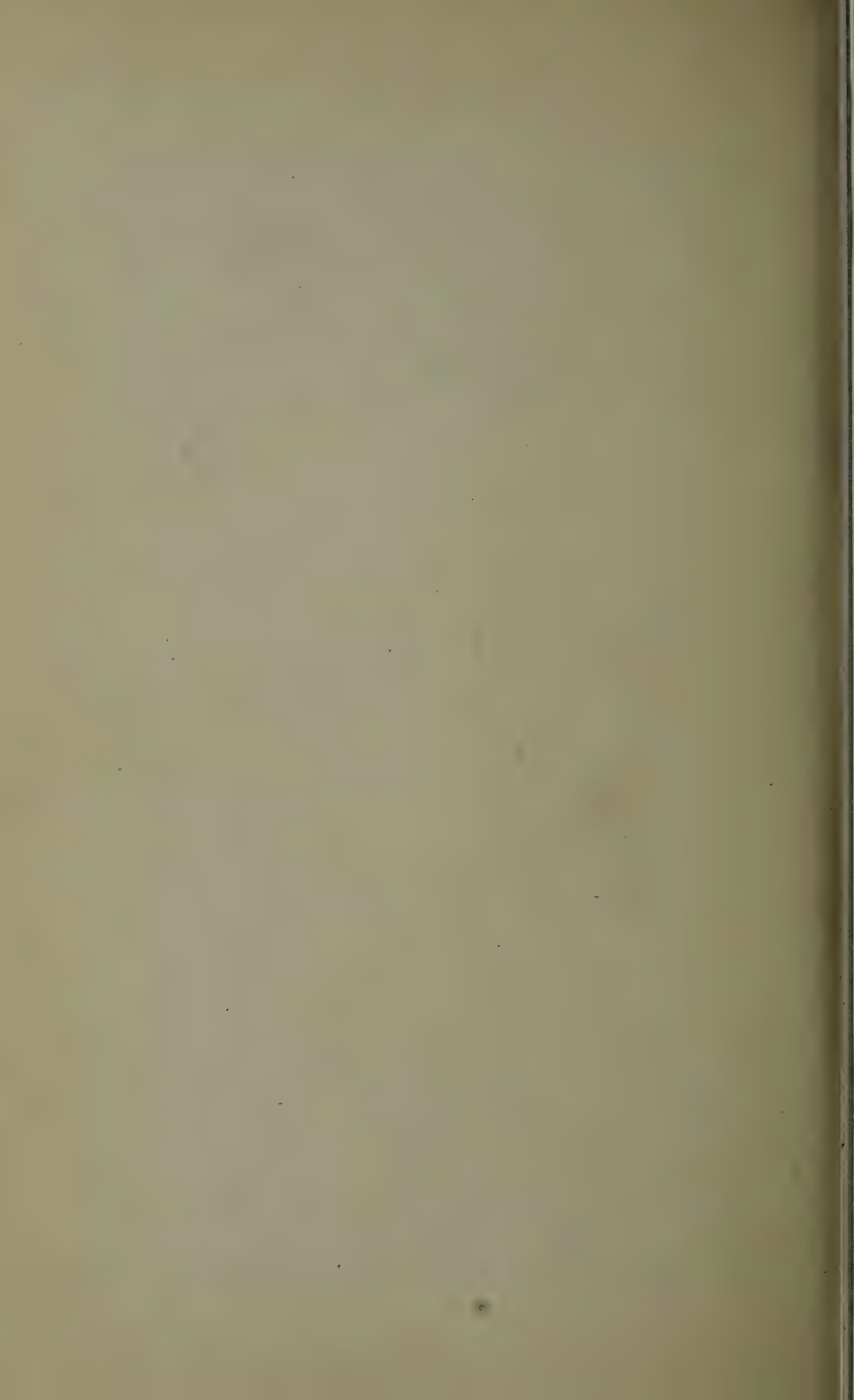
From 1860 to 1864, the demand for tin exceeded the production, and consequently prices ruled high. In 1872 the price was as much as £159 per ton. The large yield of the Australian mines from 1872 to 1878 brought the price down to £52 in the latter year. Since then, however, the Australian output has diminished, but the supply from the Straits has augmented. The demand has also increased, and prices have been £110 in January 1887, and £167 in January 1888. In March 1897 it was £60, and slowly rose up to £146 in September 1899; from this date to September 1905 it fluctuated between £113 and £144. It then rose and reached £196 in December 1906, from which figure it has slowly receded until now (May 1910) it is £150 per ton.

Better plant and the revolution in the price of iron has caused the production of tin plates to be much increased for the same price during recent years. There are no absolutely reliable figures available as to the output of tin-plate in Wales, but it is estimated by the *Ironmonger* at 650,000 tons, requiring 11,600 tons of tin. The production of tin-plate in the United States was about 600,000 tons in 1907, requiring 10,800 tons of tin. Consequently the tin-plate trade of Wales and the United States consumed approximately 22,400 tons of tin out of a world's production of about 100,000 tons.

The price of mercury in 1874 was £26 per flask. In 1884 it fell to £5, 2s., and in 1888 it rose to £10, 7s. The decline in price of this metal was due to the increased production of California, which yielded 30,000 flasks in 1870, and 80,000 flasks in 1877. The demand for mercury in the treatment of silver ores is diminishing on account of the more general adoption of other methods for extracting silver. In 1897 it was about £7 per flask (of from 70-80 lbs.), and has since varied between this and £10.

The annual supply of silver increased from 1872 to 1885 from 50,275,000 oz. to 95,908,000 oz., and during the same period the price of the metal fell very considerably. It was in 1890 4s. 3d. per ounce; but the author pointed out in the first edition of this book (in 1890) that, as the cost of production of the metal does

not exceed 1s. 8d. per ounce, it was very probable that its market value would again fall considerably below that rate. He also stated that its market price might have been expected to fall below the lowest point actually reached had it not been for the artificial stimulus imparted by coinage legislation in the United States of America. This stimulus has since been removed, and in February 1894 silver fell to 2s. 5½d. an ounce, the lowest price it had ever touched. In August 1897 it fell to 23¾d. an ounce, but after that it steadily rose, and the average price in London during the year 1900 was 28·17d. per ounce; in 1902 it was again low, 24d., and has since varied between this figure and 30d.





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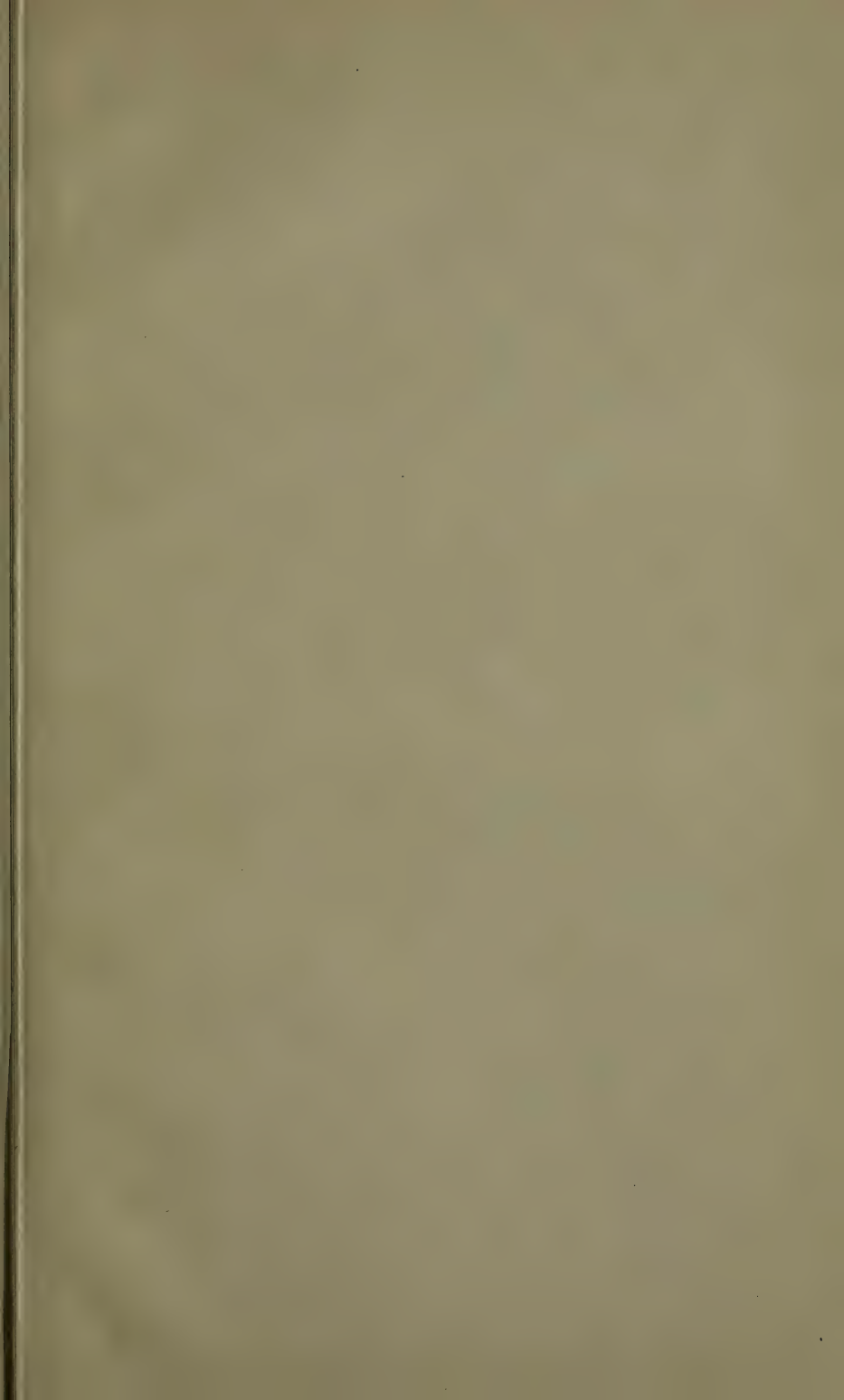
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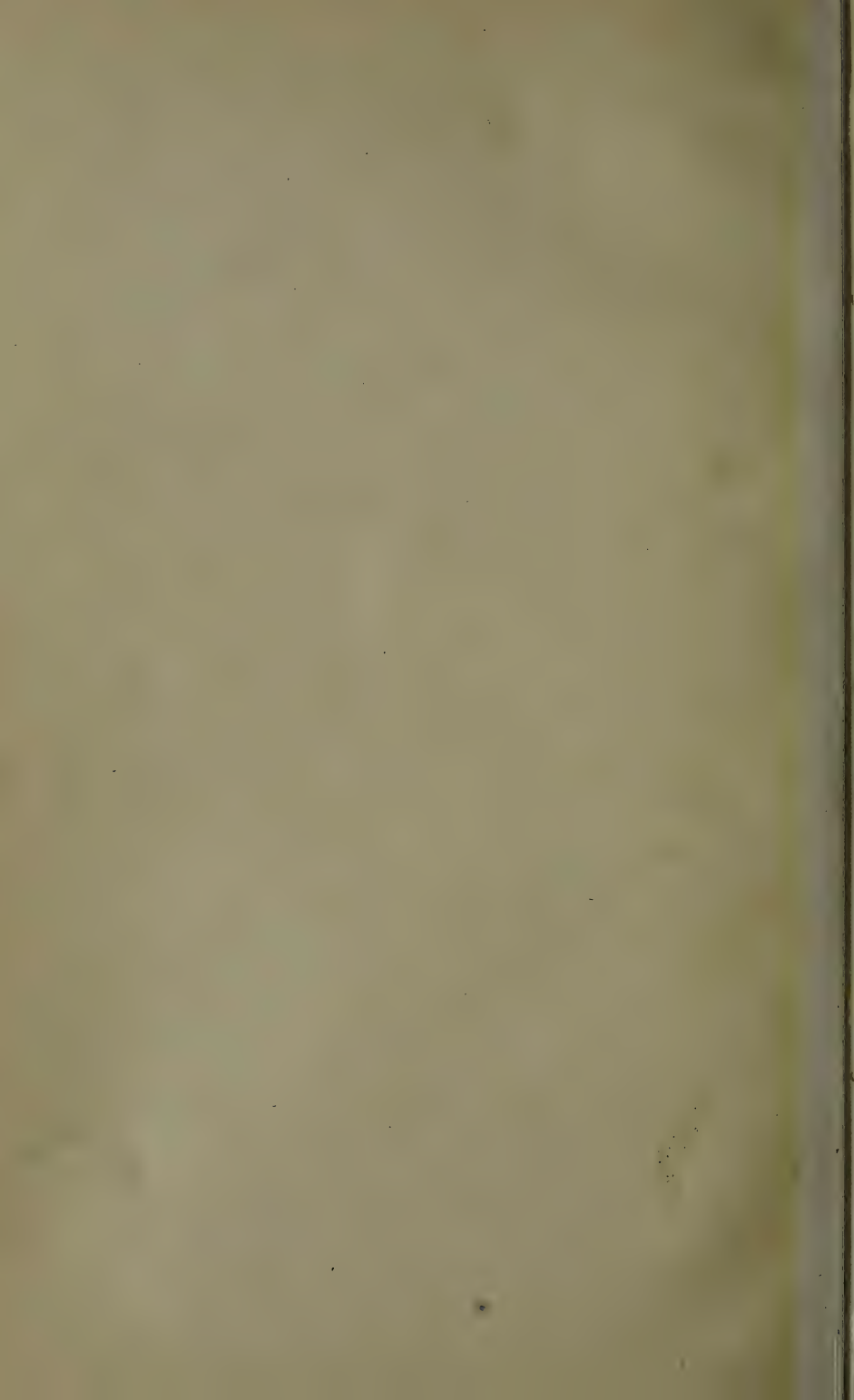
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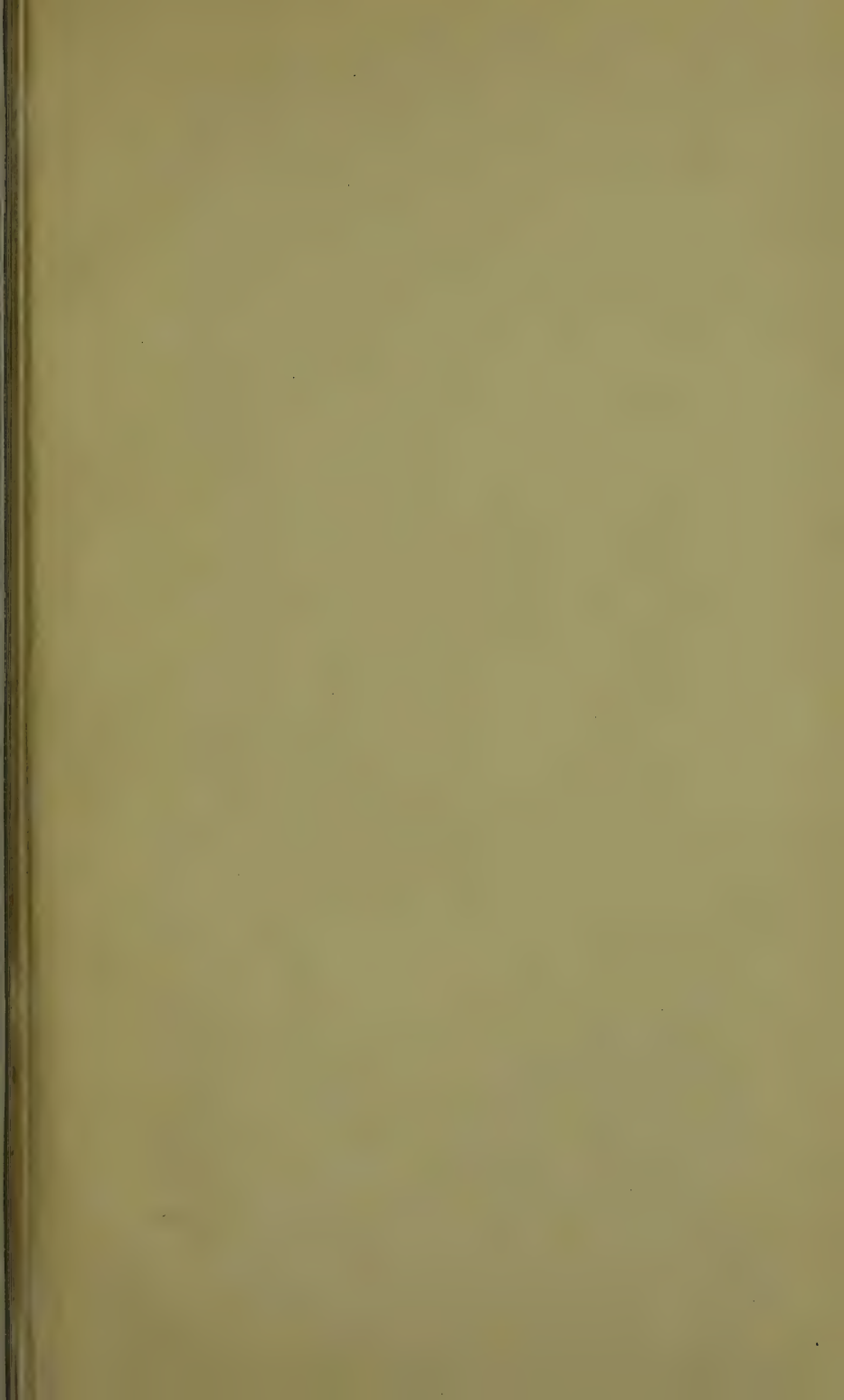
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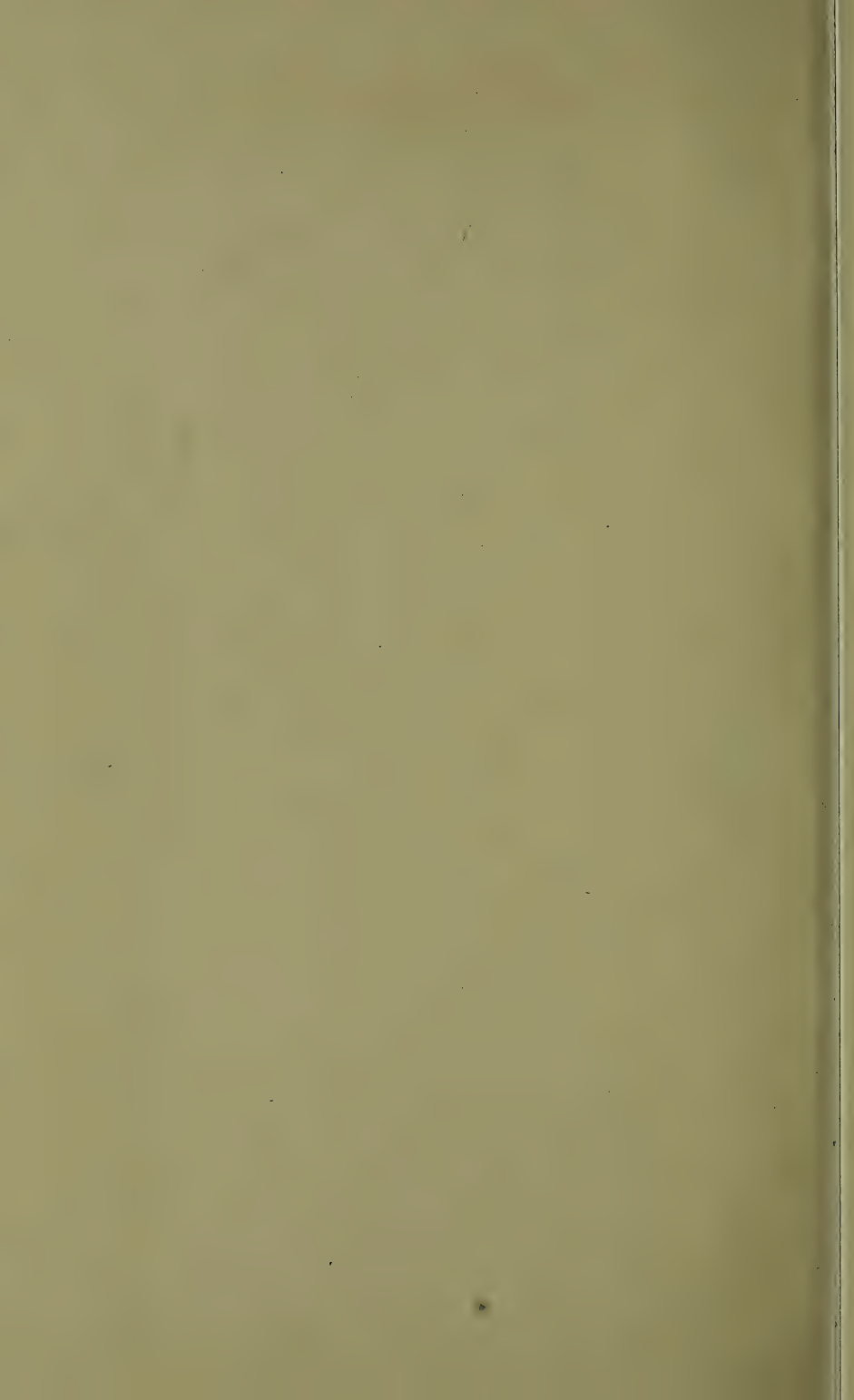
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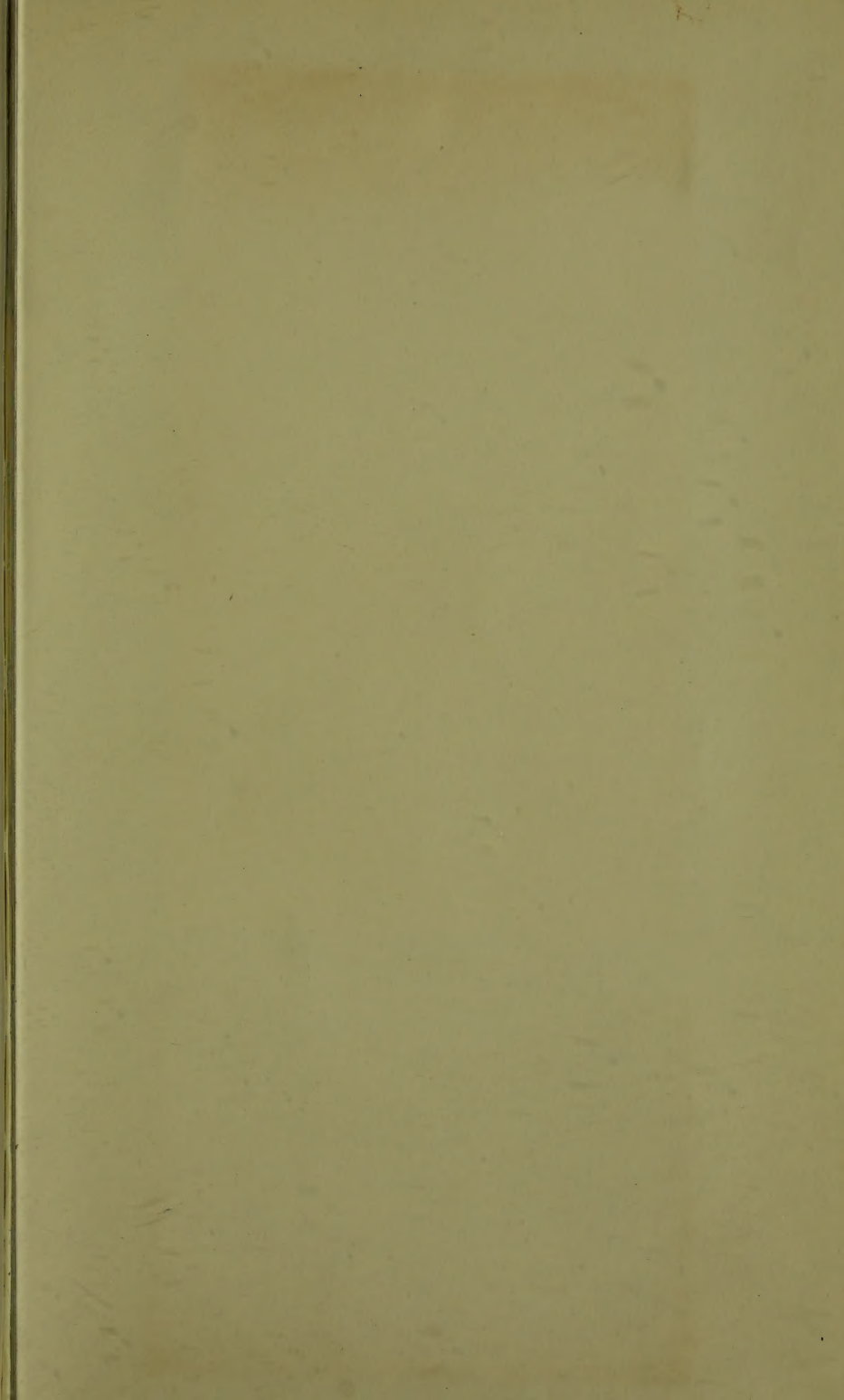












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